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Photoelectron spectroscopy study of Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ and the effect of additional Ag adatoms

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High-resolution core-level spectroscopy has been applied to the Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ surface. The Si 2*p* line shape is found to depend critically on the presence of additional Ag adatoms on the surface. A significant broadening caused by the surplus of Ag atoms could be eliminated by careful annealing. The resulting Si 2*p* spectra are significantly sharper than any published data for this or other Si based surface systems. Two major surface components are identified for the $\sqrt{3}\times\sqrt{3}$ surface, which find a natural explanation in terms of the honeycomb-chained-trimer model. A small but characteristic contribution to the Si 2*p* spectrum of the Ag/ $\sqrt{3}\times\sqrt{3}$ surface is tentatively assigned to defects.

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Various metal induced reconstructions on semiconductor surfaces provide model systems for the study of one- and two-dimensional phenomena. One such system, which exhibits a high degree of structural order is the Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ surface. The interest in this overlayer system is partly based on the somewhat complicated atomic structure, and the occurrence of Ag induced superstructures on top of the $\sqrt{3}\times\sqrt{3}$ surface. At low temperature, the addition of small amounts of Ag atoms makes the surface go through the $\sqrt{3}\times\sqrt{3}-\sqrt{21}\times\sqrt{21}-6\times6$ reconstruction series. The interest in the electronic structures of these phases has been triggered, to a large extent, by the anomalously high surface conductance value of the $\sqrt{21}\times\sqrt{21}$ surface.¹ Further, the surface electronic structure depends critically on the reconstruction, i.e., on the amount of extra Ag atoms. The $\sqrt{3}\times\sqrt{3}$ surface, which is intrinsically semiconducting, transforms into a metallic $\sqrt{21}\times\sqrt{21}$ phase when Ag is added. Further addition of Ag makes the $\sqrt{21}\times\sqrt{21}$ change into a semiconducting 6×6 surface.² The presence of additional Ag atoms does not only play an important role for the ordered, low-temperature, phases, but also at room temperature there is a significant effect on the surface electronic structure near the Fermi level. A small amount of additional Ag atoms (on the order of a few % of a monolayer) results in a partially occupied dispersing surface state band as observed by angle-resolved photoemission.^{3,4} This observation can be explained by a donation of the outermost *s* electrons of the Ag atoms to a surface state band which is intrinsic to the $\sqrt{3}\times\sqrt{3}$ reconstruction (unoccupied if there are no extra Ag adatoms). Since the Ag adatoms have a strong influence on the surface band structure they may also have significant effects on the results of other surface sensitive studies hampering investigations of the true character of the $\sqrt{3}\times\sqrt{3}$ surface.

In this study we have paid special attention to the extra Ag adatoms and what effect they may have on the Si 2*p* core-level spectra obtained by high-resolution photoelectron spectroscopy. It is found that extra Ag adatoms cause a broadening of the Si 2*p* core-level spectra and by eliminating them we obtained amazingly well-resolved spectra. These spectra should represent the intrinsic Ag/ $\sqrt{3}\times\sqrt{3}$ surface while spectra in the literature are broader and therefore

seem to be affected by the presence of additional Ag atoms to a significant extent.⁵⁻⁷ Our Si 2*p* core-level spectra of the Ag/ $\sqrt{3}\times\sqrt{3}$ surface show two major surface shifted components that find a natural explanation in terms of a honeycomb-chained-trimer (HCT) structure.⁸⁻¹⁰ The importance of the surface preparation and characterization is stressed in this paper.

The photoelectron spectra were measured at beam line (BL) 22 and BL I311 at the MAX-lab synchrotron radiation facility in Lund, Sweden. Large hemispherical analyzers (Scienta) were used at both beam lines. The Si 2*p* spectra were recorded in normal emission with an acceptance angle of about 15°. The energy resolution was about 70 meV at BL 22 and about 20 meV at BL I311. Spectra were also recorded in the angle-resolved mode at BL I311 with an energy resolution of ≈ 60 meV and an angle resolution of $\approx 0.5^\circ$. All spectra presented here were obtained at a sample temperature of approximately 100 K. Si(111) samples cut from an Sb-doped (3 Ω cm) wafer were used at both experimental stations. The samples were cleaned by an etching method before they were put into the ultrahigh vacuum system. The *in situ* cleaning of the Si samples was performed by direct current heating. Annealing temperatures up to approximately 940 or 1200 °C have been used with equally good results as evidenced by the quality of the Si 2*p* core-level spectra. The Si(111) 7×7 surface formed after the *in situ* cleaning process was exposed to Ag from a filament source to form the Ag/ $\sqrt{3}\times\sqrt{3}$ reconstruction. A quartz crystal thickness monitor was used to measure the evaporation rate. In this study we present data from three different preparations.

(1) An Ag rich surface was prepared by evaporating 1.2 ML on a 7×7 surface at $\approx 500^\circ\text{C}$. After a 1 min anneal at $\approx 540^\circ\text{C}$ another 0.6 ML of Ag was added at $\approx 500^\circ\text{C}$.

(2) 1.2 ML of Ag was evaporated at a sample temperature of $\approx 520^\circ\text{C}$ followed by a 2 min anneal at $\approx 540^\circ\text{C}$. This amount of Ag was chosen as a compromise between having enough Ag to form a complete $\sqrt{3}\times\sqrt{3}$ reconstruction (1 ML) and trying to minimize the surplus of Ag on the surface.

(3) By annealing the surface described in (2) at $\approx 600^\circ\text{C}$ for 2 + 2 min the number of extra Ag atoms was substantially reduced. All three surface preparations showed excellent $\sqrt{3}\times\sqrt{3}$ low-energy electron diffraction (LEED) patterns.

FIG. 1. Si 2*p* spectra obtained at a sample temperature of ≈ 100 K for three different preparations of the Ag/ $\sqrt{3}\times\sqrt{3}$ surface. Spectrum (a) was measured from a surface exposed to 1.8 ML of Ag annealed at $\approx 540^\circ\text{C}$ [prep. (1)]. The surface in (b) was formed from a 1.2 ML coverage of Ag that was annealed at $\approx 540^\circ\text{C}$ [prep. (2)]. Subsequent annealing of the surface in (b), at $\approx 600^\circ\text{C}$ [prep. (3)], resulted in the well-resolved spectrum shown in (c).

Si 2*p* spectra obtained from the three different preparations of the Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ surface are shown in Fig. 1. Based on the LEED patterns alone it is not possible to distinguish between the preparations, but as revealed by Fig. 1 the core-level spectra look quite different. Spectrum (a) was obtained at BL 22 from a surface prepared from a total Ag exposure of 1.8 ML [prep. (1)]. This surface preparation is bound to result in a $\sqrt{3}\times\sqrt{3}$ surface with a surplus of Ag atoms. The Si 2*p* spectrum of this surface is rather broad, but the existence of at least two components is evident from the raw data. The general shape of the spectrum is quite similar to spectra in the literature.^{6,7} This is particularly evident in the case of the low-temperature spectrum obtained at a similar energy resolution by Le Lay *et al.*⁷ In that study the surface was prepared by evaporating a few ML of Ag and annealing at 500°C . Since one ML is enough to form the $\sqrt{3}\times\sqrt{3}$ reconstruction also the spectrum in Ref. 7 should represent a surface with a surplus of Ag atoms. The close resemblance between our spectrum and that of Ref. 7 results in a consistent picture of the Si 2*p* line shape for $\sqrt{3}\times\sqrt{3}$ surfaces prepared by a significant overdosage of Ag. The change of the spectral shape, as the amount of Ag is decreased, is shown by spectra (b) and (c). Spectrum (b) was measured at BL I311 from a $\sqrt{3}\times\sqrt{3}$ surface prepared according to method (2) (1.2 ML of Ag). This preparation clearly results in a spectrum that is better resolved. As a part of the improvement the tail at the low binding energy side shows a more peaklike shape.

The 1.2 ML dosage ensures that there is enough Ag to obtain a full coverage of the $\sqrt{3}\times\sqrt{3}$ reconstruction, but with the obvious drawback that there will still be a surplus of Ag atoms on the surface. These Ag atoms are known to give rise

to a highly dispersing metallic surface state band with an energy minimum near the Γ point of the $\sqrt{3}\times\sqrt{3}$ surface Brillouin zone (SBZ).^{3,4} This energy minimum moves deeper with increasing concentration of additional Ag atoms. In Fig. 2 we show angle-resolved valence-band spectra around the second $\bar{\Gamma}$ point of the $\sqrt{3}\times\sqrt{3}$ SBZ. The region around the second $\bar{\Gamma}$ point is chosen because the surface state emission is much stronger for this $k_{\parallel}$ range than near normal emission.^{3,4} These spectra show clearly the Ag induced band (*S*) which crosses the Fermi level on both sides of the $\bar{\Gamma}$ point. The small feature slightly to the left of *S* may indicate the initiation of a $\sqrt{21}\times\sqrt{21}$ -like surface band structure,² even though there was no indication of any $\sqrt{21}\times\sqrt{21}$ spots in LEED. Anyway the important conclusion from the valence-band spectra is that the $\sqrt{3}\times\sqrt{3}$ surface has additional Ag adatoms which are not intrinsic parts of the $\sqrt{3}\times\sqrt{3}$ reconstruction. Spectra 1(a) and (b) clearly show that a decrease in the Ag deposition results in a sharper Si 2*p* line shape and it is therefore desirable to obtain a preparation without any extra Ag atoms to obtain the true line shape. Since the surface state emission near the Fermi level is directly correlated to the presence of Ag adatoms we have used this contribution to the valence-band spectra as a critical monitor of the amount of additional Ag. Preparation (3), which involves a 600°C annealing for 2 + 2 min is a successful procedure to prepare a $\sqrt{3}\times\sqrt{3}$ surface which is essentially free from Ag adatoms. The valence-band spectra from this surface preparation show no emission near the Fermi level [Fig. 2(b)]. This is taken as experimental proof that the extra Ag atoms have been reduced to an insignificant amount. Under this condition one can expect the Si 2*p* core level to correctly represent the Ag/ $\sqrt{3}\times\sqrt{3}$ surface. As can be seen from Fig. 1(c) the Si 2*p* spectrum has become sharper and as a consequence clear shoulders appear at relative bindings energies of ≈ 0.1 and ≈ 0.7 eV and the small contribution on the low binding energy side has developed into a sharper feature.¹¹

Having established the line shape of what should be close to an ideal Ag/ $\sqrt{3}\times\sqrt{3}$ surface it is meaningful to decompose the core-level spectra into their different components. The 140 eV spectrum in Fig. 1(c) with its rather weak shoulders is, however, not ideal for this purpose. It turns out that the photon energy dependence of the intensities for the different components makes the 135 eV spectrum a better choice (see Fig. 3). This spectrum is extremely well resolved and the energy positions of the different components can essentially be determined directly from the raw data. A fitting procedure has nevertheless been applied in order to obtain more detailed information. A Voigt line shape (convolution of Gaussians and Lorentzians) has been used for all components. The Gaussian width was allowed to vary for the different components but the Lorentzian full width at half maximum was fixed to 80 meV which is close to what has been used in other studies.^{12,13} The fit shows three major components of which one corresponds to the bulk Si atoms (B) and the other two, *S*1 and *S*2, to Si atoms of the reconstructed layers. The tail extending toward lower binding energies is not so well resolved and the number of components is therefore a bit

FIG. 2. Angle-resolved valence-band spectra from preparations (2) and (3) measured at 100 K. The angle range corresponds to emission around the Γ point of the second $\sqrt{3}\times\sqrt{3}$ SBZ (Γ_2). Extra Ag atoms on top of the Ag/ $\sqrt{3}\times\sqrt{3}$ surface induce the surface state emission (S) near the Fermi level, in (a). Annealing at $\approx 600^\circ\text{C}$ can remove this emission as shown by the spectra in (b).

uncertain. However, it can be fitted in a satisfactory way by two components as shown in the figure. The Gaussian widths for the different components are extremely small for being a silicon based overlayer system. The bulk component, which is the sharpest, has a Gaussian width of only 65 meV. The

FIG. 3. Si 2p core-level spectrum obtained at 100 K from the same surface as in Fig. 1(c) and Fig. 2(b). The S1 and S2 surface components are shifted by 0.32 and 0.13 eV, respectively. Two small components appear at -0.20 and -0.27 eV.

FIG. 4. Top and side view of the HCT-1 model of the Ag/ $\sqrt{3}\times\sqrt{3}$ surface. The black circles represent the Ag atoms while the other circles show positions of silicon atoms.

widths of the S1 and S2 components are 90 and 95 meV, which are also unusually small values.

The earlier core-level studies of the Ag/ $\sqrt{3}\times\sqrt{3}$ surface have not been performed on surfaces with a minimized amount of Ag adatoms. The spectra are therefore similar to spectrum (a) in Fig. 1. Since the Si 2p spectra obtained from an Ag rich $\sqrt{3}\times\sqrt{3}$ surface is appreciably broader than the spectra shown in Figs. 1(c) and 3 it is not meaningful to make a detailed comparison between our high-resolution spectra and the results in the literature. It is, however, interesting to note the similarity on the low binding energy side. A common feature of the Si 2p spectra is the pronounced tail that is present in both room-temperature spectra⁶ and spectra obtained at low temperature.⁷ The smeared out tail in these spectra becomes significantly more pronounced in the high-resolution spectra in Figs. 1(c) and 3. It seems that this low binding energy feature is characteristic of the Ag/ $\sqrt{3}\times\sqrt{3}$ surface. The very small intensity of the two components used to fit the “tail” excludes an interpretation in terms of Si atoms of the $\sqrt{3}\times\sqrt{3}$ reconstruction itself. A plausible explanation could be “intrinsic” defects, like $\sqrt{3}\times\sqrt{3}$ domain boundaries.¹

There is a general consensus that the Ag/ $\sqrt{3}\times\sqrt{3}$ surface is arranged according to the HCT model. A few slightly different versions of this model have been suggested.^{8–10} In Fig. 4 we show the HCT-1 model from Ref. 10 which shows the essential features of this class of models for the Ag/ $\sqrt{3}\times\sqrt{3}$ surface. In this structure the top Si layer is missing and the Ag atoms as well as the uppermost 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 bulklike environment and may not give rise to any significant shift of the Si $2p$ core level. The spectrum in Fig. 3 consists of one bulk component and two major surface contributions S1 and S2. The surface components find a natural explanation in terms of the Si trimer atoms and the second layer Si atoms, respectively.

In a recent scanning tunneling microscopy study of the $\text{Ag}/\sqrt{3}\times\sqrt{3}$ surface at 62 K it was found that the $\sqrt{3}\times\sqrt{3}$ unit cell has an asymmetric appearance in contrast to what is observed at room temperature.¹⁴ A transition from a surface described by the HCT model at room temperature to an asymmetric modification described by the inequivalent triangle (IET) model was proposed to occur at low temperature. The transition temperature is, however, unknown but the low-temperature phase seems to be well developed at 62 K.¹⁴ For the above discussion of the Si $2p$ spectra it would, of course, be interesting to know if the surface has gone through this phase transition at 100 K, but there is no qualitative difference expected from the IET model. The asymmetry is related to a change of the Ag atom positions while it does not affect the equivalency among the surface and second layer Si atoms, respectively. Theoretical studies of the surface band structure for the HCT and IET models provide, however, information that can be used to determine which reconstruction is present on the surface.¹⁴ In Fig. 2 there are two occupied surface state bands around 1 eV below the Fermi level. These bands are degenerate at the K point as shown by the photoemission study of Johansson *et al.*³ This

degeneracy is also reproduced in the calculations based on the HCT model.¹⁴ The calculations of the IET predict that the degeneracy is lifted and that the two bands split by 0.15 eV. We have looked for the splitting in the surface state bands both at 100 and 70 K without any positive result.² We therefore have to conclude that there is no sign of the asymmetric $\sqrt{3}\times\sqrt{3}$ unit cell in the temperature range investigated in our photoemission studies. Based on this observation we find that a comparison between our Si $2p$ data and the HCT model is most reasonable.

In summary, we have shown that a small amount of extrinsic defects can have a significant effect on the Si $2p$ line shape. Our results stress the importance of a detailed sample characterization. Just a high-quality LEED pattern is not enough to define the surface quality in this case. A tiny amount of additional atoms, which is invisible to most surface science techniques, results in a substantial broadening of the Si $2p$ spectra. In the Ag/Si case we have the rather fortunate situation that the extra Ag atoms reveal themselves by a characteristic surface state emission in the valence band. By preparing a sample without this surface state emission Si $2p$ spectra consisting of exceptionally narrow components were obtained from the $\text{Ag}/\sqrt{3}\times\sqrt{3}$ surface. The two real surface components can both be explained by the HCT model of the $\text{Ag}/\sqrt{3}\times\sqrt{3}$ surface.

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¹¹Si $2p$ spectra of almost the same quality as the spectrum in Fig. 1(c) have been obtained at BL 22 as well. This means that the different line shapes in Fig. 1 are not a result of the difference in the energy resolution.

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