Surface and Bulk Core-Level Shifts of the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag Surface: Evidence for a Charged $\sqrt{3}\times\sqrt{3}$ Layer

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Si $2p$ and Ag $4d$ photoelectron spectra have been measured for the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface at both surface- and bulk-sensitive photon energies. A dramatic shift of the bulk Si $2p$ component for the $\sqrt{3}\times\sqrt{3}$ surface has been observed and is attributed to the presence of an inherently charged $\sqrt{3}\times\sqrt{3}$ layer. A single component of surface Si $2p$ levels is found for the $\sqrt{3}\times\sqrt{3}$ surface. Discussion of structural and growth models of the $\sqrt{3}$-Ag surface is made.

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The Si(111)$\sqrt{3}\times\sqrt{3}$-Ag ($\sqrt{3}$-Ag in short) surface is a prototypical metal-semiconductor submonolayer interface that has been attracting much attention.[1] However, this surface has turned out to be one of the most mysterious surfaces.[2,3] The saturation Ag coverage for the $\sqrt{3}$-Ag is still controversial and the surface atomic geometry is not well established although many workers have agreed that the Ag atoms are embedded below the first Si layer.[3]

Separation of surface core levels from bulk core levels has been reported for many single-crystal surfaces, which is very indicative of the properties of the surfaces.[4] In this Letter, we report on a synchrotron-radiation photoemission study of the $\sqrt{3}$-Ag and Si(111)7×7 surfaces.

The experiments were performed on beam line BL-11D[5] of the Photon Factory, the National Laboratory for High Energy Physics. Monochromatized photon beams in the energy range of 20–140 eV were used at energy resolutions (ΔE) of 0.1–0.3 eV FWHM and a double-pass cylindrical mirror analyzer was used at $\Delta E=0.1$ eV. This gave the total ΔE of ∼0.2–0.4 eV.

A Si(111) wafer (phosphorus doped, 10–15 Ω cm, $4\times20\times0.15$ mm^3) was preoxidized and cleaned *in situ* by direct-current heating at ∼1150 °C under a base pressure of $\sim2\times10^{-10}$ Torr. After the cleaning, a clear 7×7 LEED pattern was observed and a clear metallic surface state was observed in valence-band spectra, which is an indication of a good 7×7 surface.[6] 99.999% pure Ag was deposited onto the heated substrate (∼400 °C) from a Mo spiral filament at a deposition rate of roughly 0.13 ML/min; 1 ML (monolayer) is defined to be 7.8×10^{14} cm^{-2}, the ideal surface Si density.

Figures 1 and 2 show the evolution of Si $2p$ spectra with the increase in Ag coverage for $h\nu=108$- and 130-eV synchrotron radiation, respectively. The dots are actual data points with the cubic background curve subtracted and normalized at the highest peak. Duration of Ag deposition is indicated on the left and observed LEED patterns are on the right. The experimental data were fitted with linear combinations of the Voigt functions in which the Gaussian and Lorentzian linewidths are common fitting parameters.

The dashed and dot-dashed curves in Figs. 1 and 2 are surface and bulk components, respectively, and the vertical (dashed and solid) bars indicate locations and relative heights of the component core levels. The solid curves are the sum of the surface and bulk contributions which fit the experiments very well. The fitting parame-

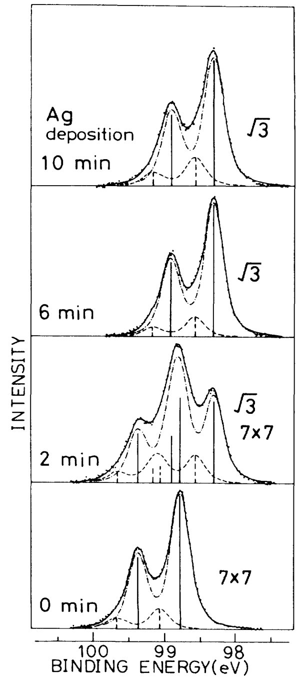

FIG. 1. Evolution of Si $2p$ photoelectron spectra with increase in Ag coverage for 108-eV synchrotron radiation (see text). The spectra are bulk sensitive because of the low electron kinetic energy of ∼5 eV.

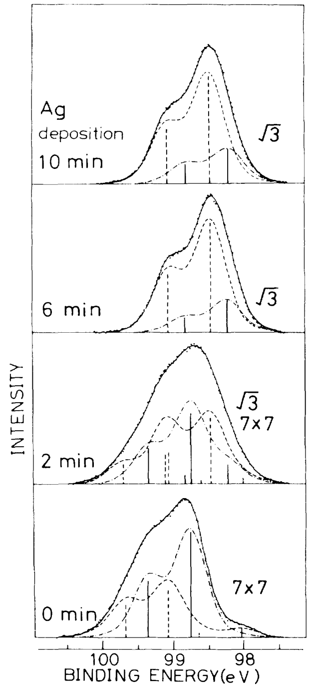

FIG. 2. As in Fig. 1 but for 130-eV radiation. The spectra are surface sensitive because of the electron kinetic energy of ~27 eV.

ters are listed in Table I. The spectra for the 2-min Ag deposition in Figs. 1 and 2 are fitted by superposing the spectra for the 7×7 and $\sqrt{3}$-Ag at 6 min. The spectra and fitting parameters for the 7×7 surface are essentially in agreement with the corresponding parameters reported by Miller, Hsieh, and Chiang.[7] The intensity ratios of the surface peak to bulk peak are dependent on measurement geometry. In the present case, the incident light is at 45° from the surface normal and perpendicular to the axis of the cylindrical-mirror analyzer. For the $\sqrt{3}$-Ag surface in Fig. 2, the intensity ratio of the surface peak to bulk peak is very high. This implies that the mean free path (λ) of electron in the $\sqrt{3}$-Ag layer is very short. It can be roughly estimated that λ can be ~3 Å if one assumes the thickness of the $\sqrt{3}$-Ag layer of ~3 Å and the electron mean free path in the bulk Si of ~5 Å and mean emission angle of ~45°.

From the results in Figs. 1 and 2 and Table I, the following major findings can be deduced for the $\sqrt{3}$-Ag surface. (1) The Fermi level (E_F) for the $\sqrt{3}$-Ag surface is shifted toward the top of the bulk valence band (VB) by ~0.5 eV as compared with that for the 7×7 surface, which is judged from the shift of bulk Si 2p levels.[8] (2) The $\sqrt{3}$-Ag surface has only a single component of surface Si 2p levels. (3) There is no intermediate surface stage from 7×7 to $\sqrt{3}$-Ag; the $\sqrt{3}$-Ag surface grows as domains leaving the rest of the area as 7×7. These are explained further in order.

The first finding is very indicative. It is known from photoemission[6] and inverse photoemission[9] studies that the $\sqrt{3}$-Ag surface is semiconducting and there are no surface states inside the bulk band gap. Further, the Fermi pinning position for the 7×7 surface is known to be about 0.6 eV from the top of the VB.[8] These facts together with the finding (1) mean that E_F at the $\sqrt{3}$-Ag surface is almost at the top of the VB and the driving force for this pinning position can only be understood if the semiconducting $\sqrt{3}$-Ag layer is charged negatively.

A more precise description of the situation is given with the aid of Fig. 3(a). The E_F in the bulk lies at ~0.8 eV from the top of the bulk VB for the present Si wafer.[10] Two occupied surface-state bands[6] lie at ~0.8 and ~1.0–1.5 eV below E_F as illustrated in Fig. 3(a) and an unoccupied surface-state band[9] at ~2.1 eV above E_F. In order for the band bending to be upward, the $\sqrt{3}$-Ag layer must be negatively charged. For a semiconductive surface layer, the charge in the $\sqrt{3}\times\sqrt{3}$ unit cell cannot be fractional unless E_F pinning is due to defects. The possibility of defect-induced E_F pinning is excluded since the $\sqrt{3}$-Ag surface is an ordered surface and a large fraction of the surface is covered with the $\sqrt{3}$-Ag domains.[11] In fact, if the charge were defect-induced, the E_F pinning position would be Ag-coverage dependent, which is not the case. This finding is striking in that the conservation of valence electrons is broken in the $\sqrt{3}$-Ag layer, whereas in other ordered surface layers established so far, the conservation of valence electrons holds.[12] Since the charge at the $\sqrt{3}$-Ag layer is at least a

TABLE I. Fitting parameters for Si 2p spectra in Figs. 1 and 2. The parameters are self-explanatory. A positive shift represents a shift to higher binding energy side. Energies are in electronvolts and spin-orbit splittings are fixed at 0.60 eV. The increase in the Gaussian FWHM for $h\nu = 130$ eV is due to a degradation in the energy resolution of the monochromator.

Surface	Photon energy	Gaussian FWHM	Lorentzian FWHM	Branching ratio Surface	Branching ratio Bulk	Surface core-level shifts	Bulk core-level shift
7×7	108	0.21	0.18	0.50	0.54	0.30	0.0
	130	0.42	0.18	0.60	0.53	0.32, −0.72	0.0
$\sqrt{3}$-Ag (6 min)	108	0.21	0.18	0.48	0.56	0.26	−0.48
	130	0.44	0.16	0.53	0.46	0.24	−0.50

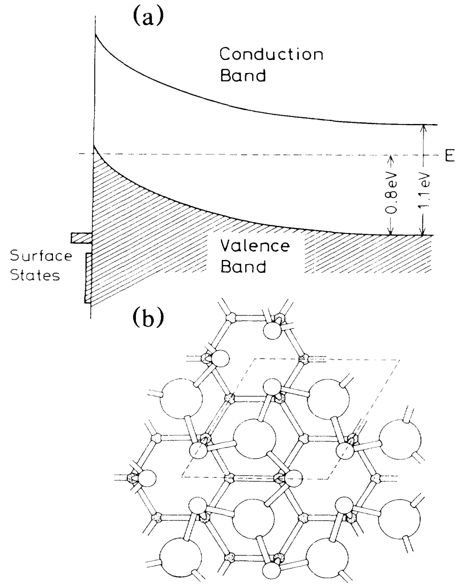

FIG. 3. (a) Schematic illustration of the Fermi-level pinning and band bending around the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface. (b) Ball-and-stick model of the $\sqrt{3}$-Ag surface (Ref. 3). Large and small open circles represent Ag and first-layer Si atoms, respectively, for the honeycomb model. For the triplet model, Ag and Si atoms are interchanged. Shaded circles are Si atoms forming a double layer. $\sqrt{3}\times\sqrt{3}$ unit cell is indicated with dashed lines.

unit charge per $\sqrt{3}\times\sqrt{3}$ cell, the compensating positive charge should be provided from the VB holes. Therefore, E_F at the $\sqrt{3}$-Ag layer must lie below the top of the VB as illustrated in Fig. 3(a). The VB hole density can be about 10^{20} cm^{-3} if E_F is just below the top of the VB.[10] Then, the thickness of the depletion layer may be on the order of hundreds of angstroms in order to compensate the negative charge at the $\sqrt{3}$-Ag layer. The rest of the band bending should be caused by ionized donors.

The finding (2) deserves further consideration. In the unit cell of the $\sqrt{3}$-Ag surface, the number of Ag atoms is 2 or 3 [as discussed later and cf. Fig. 3(b)]. The number of Si atoms involved in the $\sqrt{3}$-Ag layer is not known but would be 6 at most for the reason given below. The surface Si atoms can be divided into two groups; first group, at the surface and bound both to the Ag atoms and to the second group of Si atoms; second, near the surface but bound both to the Ag atoms and to the otherwise dangling bonds of the Si atoms underneath the $\sqrt{3}$-Ag layer. The possibility of having deeper Si layers that differ from the essential bulk configuration should be much less. The number of the second-group Si atoms should be 3 in the $\sqrt{3}\times\sqrt{3}$ unit cell. The number of the first group would be 2(3) if the number of Ag atoms is 3(2) because of the geometrical limitation.[3] The finding (2) implies, therefore, either that there is only the first-group Si or that there are the first and second groups of Si but both have similar $2p$ surface core-level shifts. However, the chemical environments for the first- and second-group Si atoms are different and the core-level shifts would appear to be different. Theoretical investigation is needed on this point. It is worthwhile to note here that Hanawa, Fukuda, and Watamori[13] have recently performed LEED/constant momentum transfer average analysis of the $\sqrt{3}$-Ag surface. They found improvement in the agreement of I-V profiles between theory and experiment if they used surface models in which the second kind of Si layer is removed.

There have been several proposals for the structure of the $\sqrt{3}$-Ag surface.[3] Kono, Higashiyama, and Sagawa[3] were the first to abandon the model based on the presence of a surface Si double layer and proposed two plausible models in which only the first kind of surface Si atoms is present. The two models proposed are illustrated in Fig. 3(b) and they are a honeycomb model ($\theta=\frac{2}{3}$ ML, θ being the saturation coverage) and a triplet model ($\theta=1$ ML). In the honeycomb model, the $\sqrt{3}$-Ag layer contains two Ag and three Si surface atoms in the $\sqrt{3}$ unit cell and in the triplet model, three Ag and two Si surface atoms. By counting of the number of valence electrons available for surface states, it can be said that the honeycomb-model surface is metallic [3(dangling bond) + 3 × 4(Si $3s,3p$) + 2 × 1(Ag $4s$) = 17 electrons] and that the triplet-model surface is semiconducting [3(dangling bond) + 2 × 4(Si $3s,3p$) + 3 × 1(Ag $4s$) = 14 electrons] if the $\sqrt{3}$-Ag layer is not charged. However, the $\sqrt{3}$-Ag layer is found to be negatively charged and it would be more likely to have the honeycomb $\sqrt{3}$-Ag layer negatively charged by 1 electron per $\sqrt{3}$ unit cell than the triplet $\sqrt{3}$-Ag layer negatively charged by 2 electrons per $\sqrt{3}$ unit.

Very recently, two papers on scanning tunneling microscopy (STM) studies of the $\sqrt{3}$-Ag surface appeared.[14,15] For both studies, a honeycomb arrangement of either Ag or Si atoms is indeed observed. Van Loenen *et al.*[14] concluded the honeycomb to be due to Si atoms primarily because of the conservation of valence electrons and the semiconductive nature of the $\sqrt{3}$-Ag surface. As already described, the conservation of valence electrons does not hold for the $\sqrt{3}$-Ag surface. Further, a proposed structural model (Fig. 4 in Ref. 14) has two types of surface Si atoms, which seems to be inconsistent with the present finding (2). Wilson and Chiang,[15] on the other hand, concluded without sound basis that the honeycomb bright spots in their STM image are due to individual Ag atoms and therefore the saturation coverage is precisely $\frac{2}{3}$ ML. Our discussion about the saturation coverage is found below.

We now explain the conclusion (3) and proceed to further discussion. As mentioned, the spectra for 2-min Ag deposition in Figs. 1 and 2 are fitted literally by simple superposition of the spectra for the 7×7 and the $\sqrt{3}$-Ag surfaces. This means that Ag atoms deposited onto the heated substrate migrate over the surface and form domains of $\sqrt{3}$-Ag layer leaving the rest as 7×7 surface. The domain width of the $\sqrt{3}$-Ag should become comparable to or larger than the coherence length of the LEED electron beam (typically on the order of 100 Å) by the time the $\sqrt{3}$ LEED pattern becomes visible since the $\sqrt{3}\times\sqrt{3}$ LEED spot size was always comparable to that of the LEED electron gun. The domains would probably start to grow at steps on the surface.

Even if Ag atoms are deposited for more than 6 min, the Si $2p$ spectra in Figs. 1 and 2 (shown for 10 min) do not show essential changes from the 6-min spectra. This is the result of the well-known Stranski-Krastanov growth of the Ag/Si(111) system at moderate temperatures. Namely, the Ag islands which formed after the completion of the $\sqrt{3}$-Ag layer have very little surface area, and thus no changes can be noticed in the spectra.[16] However, one specific issue should be discussed here, i.e, at what coverage the $\sqrt{3}$-Ag completes and at what coverage the Ag islands start to grow.[3] We therefore measured Ag $4d$ photoelectron spectra for $h\nu=60$ eV paying special attention to their behavior as a function of the duration of Ag deposition. The result showed that the Ag $4d$ spectra are invariant up to 6 min deposition but changed slightly in going from 6 to 8 min deposition and stayed invariant afterward. We believe that the slight change is an indication of the completion of the $\frac{2}{3}$-ML honeycomb $\sqrt{3}$-Ag layer and the onset of a $\frac{1}{3}$-ML dilute Ag adatom layer[3] but not the onset of the Ag island growth. This is because the Ag islands have very small surface area that should not contribute to the spectra change, as mentioned already. If it were the effect of Ag islands it would grow further because of the increase in surface area even though it is small. In the STM studies of the $\sqrt{3}$-Ag surface,[14,15] no evidence for the dilute adatoms is found. It may be possible that the dilute Ag adatoms are so loosely bound to the $\sqrt{3}$-Ag layer that they move from the tip of the STM. Further studies are needed; however, the effects of defects and domain boundaries may destroy the argument above.

In conclusion, a dramatic bulk Si $2p$ core-level shift is found for the $\sqrt{3}$-Ag surface. From the consideration that the $\sqrt{3}$-Ag surface is semiconducting, we conclude that the $\sqrt{3}$-Ag layer is inherently negatively charged. The surface Si $2p$ component for the $\sqrt{3}$-Ag surface is found to be only one. We believe this implies a single type of surface Si atoms at the $\sqrt{3}$-Ag layer. This and the growth mode of the $\sqrt{3}$-Ag surface are discussed in favor of the honeycomb model proposed previously.[3]

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