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Correlation between surface core levels and surface states in Si(111)-(7×7) probed by Ag adsorption

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Synchrotron-radiation photoemission is employed to examine the spectral modifications caused by Ag adsorption on Si(111)-(7×7). There is a correlation between the adatom-derived surface state at a binding energy of 0.3 eV and a surface core-level component at a binding energy 0.8 eV lower than that of the bulk core-level component; both are completely suppressed at a $\frac{1}{4}$ monolayer Ag coverage. This result suggests that the same surface core-level component is derived from the adatoms.

An important application of photoemission is the study of surface atomic structure based on measurements of surface core-level shifts. For clean reconstructed surfaces, the various inequivalent surface sites may show different core-level binding energies; measurements of the shifts and the relative intensities of the core-level components allow a deduction of structural information. The chemical shifts induced by adsorbates could further provide information concerning the chemical behavior of the surfaces and the resulting adsorption geometry. Many examples exist in the literature.[1–3] Yet for Si(111)-(7×7), perhaps the most studied semiconductor surface, there remains a question concerning the assignment of the surface core-level components in relation to the surface sites. This problem is partly due to the relative complexity of this surface structure. The (7×7) reconstruction is well described by the dimer–adatom–stacking-fault model of Takayanagi.[4] Within each (7×7) unit cell, there are twelve adatoms and six rest atoms. Rest atoms are threefold-coordinated surface atoms not bonded to an adatom.[5] In the Si $2p$ core-level spectra, there is a clearly resolved surface core-level component shifted by about 0.8 eV toward lower binding energies relative to the bulk component; for brevity, this surface component will be referred to as the $S2$ component following the notation used earlier.[6,7] Some researchers believe that it is associated with the surface adatoms,[6] yet others believe that it is associated with the rest atoms.[7,8] A similar study of the closely related Ge(111)-$c(2\times8)$ surface also made the rest-atom assignment.[9] Both the adatoms and rest atoms on Si(111)-(7×7) have a dangling bond and are candidates for large surface core-level shifts. The rest-atom assignment is favored based on some theoretical considerations of charge transfer on the surface.[5] However, the relevant argument is only qualitative,[7–9] and charge transfer is not the only reason for a core-level shift. This work is an attempt to resolve this site-assignment issue. Furthermore, the approach demonstrated here can be applied to other appropriate systems for site identification.

The idea is based on the correlation between adsorbate-induced spectral modifications in site-specific surface states and the core-level component in question. Hamers *et al.*, applying a current-imaging technique using a scanning tunneling microscope, made an identification of the specific surface sites on Si(111)-(7×7) where various valence surface states are localized.[10] Thus, the three surface states at about 0.3, 0.9, and 1.8 eV binding energies are associated with the adatom dangling bonds, the rest-atom dangling bonds, and the back bonds, respectively. During the initial adsorption of Ag on Si(111)-(7×7) the adatom dangling-bond state at 0.3 eV is selectively removed and the same effect is simultaneously observed on the $S2$ core-level component. This correlation then suggests that the $S2$ core-level component is associated with the adatoms.

The photoemission experiments were conducted at the Synchrotron Radiation Center of the University of Wisconsin–Madison (Stoughton, WI) on the 1-GeV storage ring Aladdin. Synchrotron radiation was dispersed by an extended-range grasshopper monochromator. An angle-integrated geometry was employed. The Si(111)-(7×7) samples were cleaned by Ohmic heating to ~1100 °C, and the surface quality was verified not only by a sharp electron-diffraction pattern but also by the observation of strong surface-state features in the photoemission spectra. Ag was evaporated from a tungsten crucible heated with a feedback-controlled electron beam and the rate of deposition was determined by a quartz-thickness monitor. The substrate during deposition was at room temperature.

Figure 1 shows a set of Si $2p$ core-level spectra taken with a photon energy $h\nu = 160$ eV. The circles are the data points and the curves are fits to the data. The bottom spectrum is for clean Si(111)-(7×7). Its line shape has been the subject of numerous studies, and the details, available in those publications, will not be repeated here.[6–8] Briefly, the small peak at a relative binding energy of -0.8 eV indicated by the arrow is the $2p_{3/2}$ contribution of the $S2$ component. The rest of the line shape, having the appearance of a broadened spin-orbit-split peak, consists of the bulk contribution and additional surface contributions with smaller shifts. The intensities of

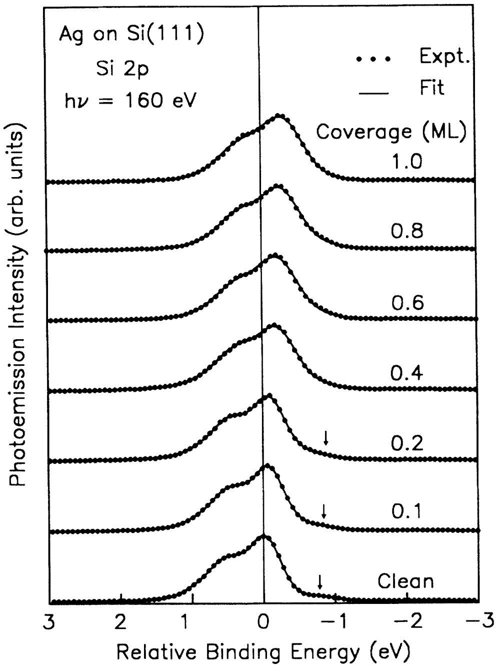

FIG. 1. Si $2p$ core-level spectra for Si(111)-(7×7) covered with various amounts of Ag as indicated. The circles are the data points and the curves are the results of a least-squares fit. The arrows indicate the $2p_{3/2}$ contribution of the $S2$ surface-shifted component. The binding-energy scale is referred to the $2p_{3/2}$ contribution of the bulk component.

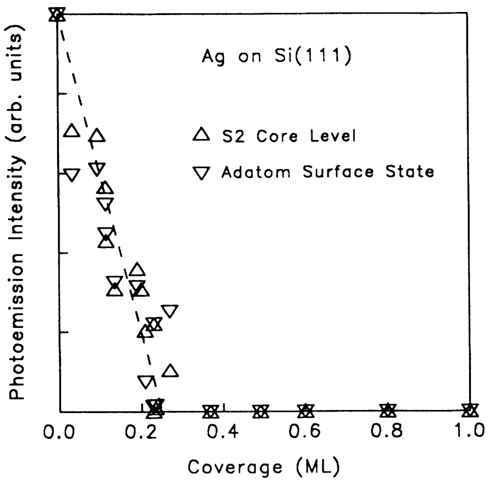

FIG. 2. The photoemission intensities of the $S2$ core-level component (triangles) and the adatom surface state (inverted triangles) as a function of the Ag coverage. The dashed straight line crossing the horizontal axis at 0.25 ML is a guide to the eye.

the $S2$ contribution can be obtained directly from the fit as discussed in previous studies. The other spectra in Fig. 1 are for Si(111) covered with various amounts of Ag as indicated. The Ag coverage is expressed in terms of monolayers (ML); 1 ML$=7.83\times10^{14}$ atoms/cm^2 is defined here as the atomic-site density for unreconstructed Si(111). The main effects of Ag adsorption can be seen to be (i) the $S2$ component is quickly suppressed, (ii) the rest of the line shape shows little change, and (iii) there is an overall shift of the entire line shape to lower binding energies due to Ag-induced changes in band bending. The intensity of the $S2$ component as a function of Ag coverage is shown in Fig. 2 by the triangles. The straight dashed line, crossing the horizontal axis at 0.25 ML, is a guide to the eye.

Figure 3 shows a set of photoemission spectra of the valence-band region taken with a photon energy of 55 eV. The bottom spectrum is for clean Si(111)-(7×7). The three peaks indicated by the inverted triangles are the aforementioned surface states associated with the adatom dangling bonds, the rest-atom dangling bonds, and the back bonds, respectively. As increasing amounts of Ag are deposited on the surface, the Ag d bands centered at about 6 eV gradually build up (data not shown). The surface-state features are also modified, as can be seen in Fig. 3. The adatom dangling-bond state at about 0.3 eV is seen to be quickly suppressed. The rest-atom dangling-bond state at about 0.9 eV appears to be broadened rather than suppressed. Although it is difficult to quantify its intensity change at higher coverages, its behavior is clearly different from that of the adatom dangling-bond state. The back-bond state appears to be broadened and somewhat shifted by the Ag adsorption.

The photoemission intensity of the adatom dangling-bond state is evaluated by subtracting a background function from each spectrum. The background function is assumed to be given by the line shape at a Ag coverage of 1

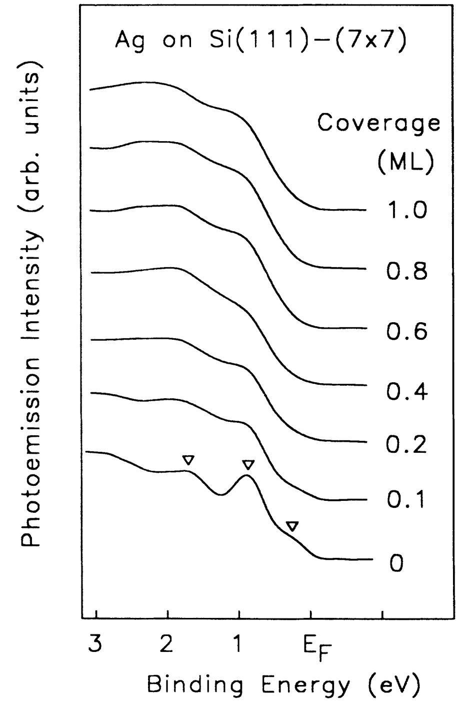

FIG. 3. Photoemission spectra of the valence-band region for Si(111)-(7×7) covered with various amounts of Ag as indicated. The binding-energy scale is referred to the Fermi level E_F. The three inverted triangles for the bottom spectrum indicate the three surface states discussed in the text.

ML. The inverted triangles in Fig. 2 indicate the intensity of this state obtained from this analysis. The triangles and inverted triangles in Fig. 2 are seen to correlate well. This suggests that the adatom dangling-bond state and the $S2$ core-level component have the same atomic origin; namely, they are both derived from the adatoms. Furthermore, both are completely suppressed at a Ag coverage of about $\frac{1}{4}$ ML, the same as the Si adatom coverage on the clean Si(111)-(7×7) surface (there are twelve adatoms per unit cell of $7\times7=49$ sites, and $\frac{12}{49}=0.245$). Thus, the interpretation is that on the average each Ag atom affects one Si adatom causing its core levels and the dangling-bond state to be modified. The Ag-Si interaction is likely to involve the saturation of the adatom dangling bond. An earlier scanning tunneling microscopy (STM) study of Ag on Si(111)-(7×7) has revealed the adsorption-induced changes on the surface,[11] yet a detailed microscopic picture of the adsorption geometry is still lacking. This problem has to do with the fact that STM does not necessarily show atoms as easily recognizable small balls on a surface and presently it is impossible to tell experimentally which atoms are being imaged. We have made STM measurements on this system as well, and the information obtained is similar to what is already available in the literature.

In the present study, Ag was chosen as the adsorbate because it shows a high degree of selectivity in attacking the site-specific surface states. Several other adsorbates have also been tried, but either they do not show the selectivity or the reaction on the surface is so disruptive that the spectral changes are too drastic for any useful conclusions to be drawn. Although the present method of site identification is an indirect method, it is our choice since single-atom core-level spectroscopic techniques have not been developed yet.

To summarize, we demonstrate here that a correlation exists between the spectral modifications of the $S2$ core-level component and the adatom surface state upon Ag adsorption on Si(111)-(7×7). This result suggests the adatom origin of the $S2$ core-level component. This method of site identification may be applied to other systems.

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