[a] Permanent address: Physics Department, Case Western Reserve University, Cleveland, Ohio 44106.

[b] Present address: Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, N. Y. 14853.

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Core-Level Binding-Energy Shifts Due to Reconstruction on the Si(111) 2 × 1 Surface

S. Brennan, J. Stöhr, and R. Jaeger

Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94305

and

J. E. Rowe

Bell Laboratories, Murray Hill, New Jersey 07974

High-resolution photoemission spectra of the Si 2p level for freshly cleaved Si(111) reveal two additional core-level structures which are shifted relative to the bulk. The observed shifts are 0.59 ± 0.04 eV to lower and 0.3 ± 0.03 eV to higher binding energy, respectively. These shifted peaks, which vanish with increasing contamination of the surface, are shown to be directly correlated with reconstruction on the Si(111) 2×1 surface.

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In metals, core-level binding-energy shifts between surface and bulk atoms have long been proposed to exist on theoretical[1] and experimental[2] grounds. Recently, photoemission measurements of the 4f core levels in the 5d metals Au,[3] W,[4] and Ir[5] have provided unambiguous proof for this effect. A key element of the proposed mechanism for surface core-level shifts in metals was the existence of tight-binding (d-like) valence-band states.[1,3]

Here, we report the observation of core-level binding-energy shifts at a semiconductor surface. Our studies on Si which has only nonlocalized s-p valence bands show that surface core-level shifts exist on more general grounds than previously assumed and that they can provide useful structural information for the technologically important semiconductor surfaces. Photoemission spectra of the Si 2p core level for a freshly cleaved Si(111) 2 × 1 surface exhibit two pronounced addi-

tional structures at lower and higher binding energy relative to the bulk. The observed shifts are different in sign and magnitude and can be directly related to charge transfer of Si atoms at the reconstructed 2 × 1 surface. In particular, the two core-level structures shifted by -0.6 eV to lower and $+0.3$ eV to higher binding energy are directly linked to the surface Si atoms which are buckled inward and outward with respect to the bulk positions.[6] Thus, a one-to-one correspondence between charge transfer, surface structure, and surface core-level shifts can be established. Since surface reconstruction and charge transfer is a common phenomenon on semiconductor surfaces the surface core-level shifts observed here have important general implications for structural investigations of other surfaces.

Experiments were performed during dedicated time (3.0 GeV, 80 mA) at the Stanford Synchrotron Radiation Laboratory with use of the Grass-

hopper monochromator equipped with a 1200-line/mm holographic grating. Spectra were recorded at $h\nu = 150$ eV by use of a double-pass cylindrical mirror analyzer (CMA) operated at a pass energy of 10 eV. The combined instrumental resolution was 350 meV. The synchrotron light was incident perpendicular to the CMA axis at an angle of about 10° from the surface of the sample. The n-type ($n = 1 \times 10^{15}$ cm^{-3}) Si single crystals were cleaved *in situ*. Spectra were recorded within minutes after cleaving to avoid effects due to contamination buildup on the surface. The base pressure in the vacuum chamber was less than 5×10^{-10} Torr.

The Si $2p$ photoemission spectra for a freshly cleaved Si(111) 2×1 surface and after exposure to 15 L (1 L $= 10^{-6}$ Torr sec) of oxygen are shown as points in Fig. 1. The "clean" upper spectrum was obtained in a single sweep immediately after
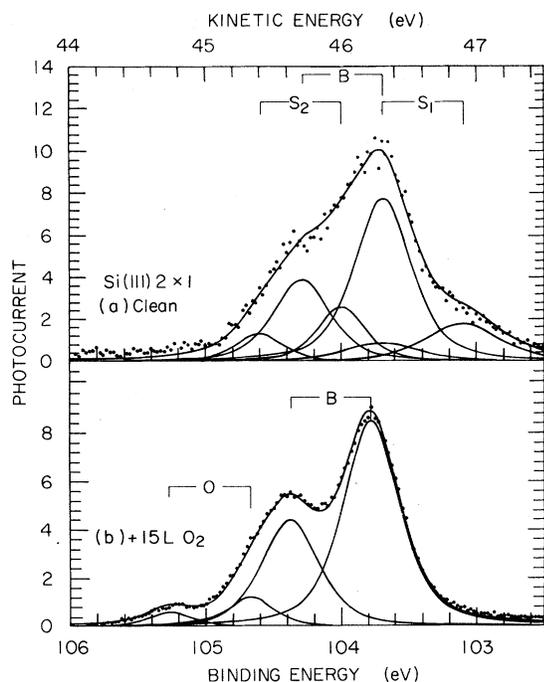
FIG. 1. (a) Si $2p$ core-level photoemission spectra (dots) recorded at $h\nu = 150$ eV for an *in situ* cleaved Si(111) surface. The solid lines denote a fit with three spin-orbit–split doublets S_2, B, and S_1 discussed in the text. Peaks B correspond to bulk Si atoms and peaks S_1 and S_2 are attributed to atoms A and B of the relaxed, buckled surface layer shown in Fig. 2(b). (b) Si $2p$ spectrum as in (a) after exposure to 15 L of unexcited oxygen. Peaks B are attributed to bulk Si atoms and peaks O to Si atoms which have transferred charge to the chemisorbed oxygen.

a cleave which produced a mirrorlike surface. Several other spectra recorded for different cleaves gave similar results. Surface cleanliness was checked by core-level photoemission spectra of the C $1s$ and O $1s$ lines using 650 eV radiation from the Grasshopper monochromator.

The spectrum obtained for the *oxygen-exposed surface* in Fig. 1(b) shows two well-defined peaks corresponding to the spin-orbit–split Si $2p_{1/2}$ and $2p_{3/2}$ levels located at kinetic energies 45.6 and 46.2 eV, respectively. We have plotted the data as a function of the measured electron kinetic energy (E_{kin}) and binding energy (E_B) relative to the vacuum level ($E_B = h\nu - E_{kin}$). In addition, we observe a weak peak around $E_{kin} = 44.7$ eV which because of its absence in the clean Si $2p$ spectrum is identified as oxygen induced. The spectrum recorded for the *clean surface* exhibits the same main two-peak structures. However, the high-kinetic-energy side shows a pronounced shoulder around $E_{kin} = 46.9$ eV. Another shoulder around $E_{kin} = 46.0$ eV fills in the spin-orbit gap of the two main peaks. With increasing surface contamination as monitored by the O $1s$ photoemission intensity a continuous transition from the "clean" to the "dirty" spectrum in Fig. 1 can be observed. It is for this reason that we have used a rather poor signal-to-noise "clean" spectrum for Fig. 1(a) which consists of a single sweep recorded immediately after cleaving. It should be noted that the "dirty" spectrum in Fig. 1(b) corresponds to about $\frac{1}{3}$-monolayer coverage only.

The spectra in Fig. 1 were analyzed by a curve-fitting program with use of a line shape which had a 50% Lorentzian and 50% Gaussian contribution. In all cases the spin-orbit–split components were required to have equal widths, a 2:1 intensity ratio and a 0.60-eV separation. The main $2p_{1/2}$ and $2p_{3/2}$ peaks labeled B which we attribute to "bulk" Si atoms were fitted with the same linewidth [0.5 eV full width at half maximum (FWHM)] in all spectra. Both spectra shown in Fig. 1 exhibited extra features which could not be accounted for by a single spin-orbit–split doublet.

For the clean surface two additional structures labeled S_1 and S_2 were needed to fit the observed spectrum. One was a spin-orbit–split doublet shifted to lower E_B by -0.59 ± 0.04 eV, the other a similar doublet shifted to higher E_B by $+0.30 \pm 0.03$ eV. The fits were most sensitive to placement of the dominant $2p_{3/2}$ components which basically account for the low–binding-energy shoulder and the filling of the main spin-orbit gap seen in Fig. 1. We attribute these two additional struc-

tures to surface Si atoms in the outermost layer. Both surface-related structures S_1 and S_2 were found to have equal intensity within a few percent but different widths of 0.67 eV and 0.41 eV FWHM, respectively. Their combined intensity is 57% of the main doublet B. The oxygen-exposed surface exhibits another spin-orbit–split doublet labeled O with 0.41 eV FWHM and shifted to higher binding energy by +0.89 ±0.03 eV as shown in Fig. 1(b). This doublet is attributed to surface Si atoms which have transferred charge to chemisorbed oxygen atoms or molecules.

Most recent discussions seem to favor the buckling model for the Si(111) 2 × 1 reconstructed surface first proposed by Haneman.[7] In this model shown in Fig. 2 the outermost plane of Si atoms in the (111) surface plane is first relaxed inwards by $d - d^* = 0.12 \pm 0.04$ Å,[8-10] with alternate rows of atoms A raised and atoms B lowered with respect to the second layer underneath. The buckling amplitude b has been estimated to be somewhere between 0.30 (Ref. 9) and 0.70 Å (Ref. 10). The charge transfer at the Si(111) surface in various geometries has been the subject of numerous calculations.[10-16]

(a) Unrelaxed 1×1

(b) Relaxed and Buckled 2 ×1
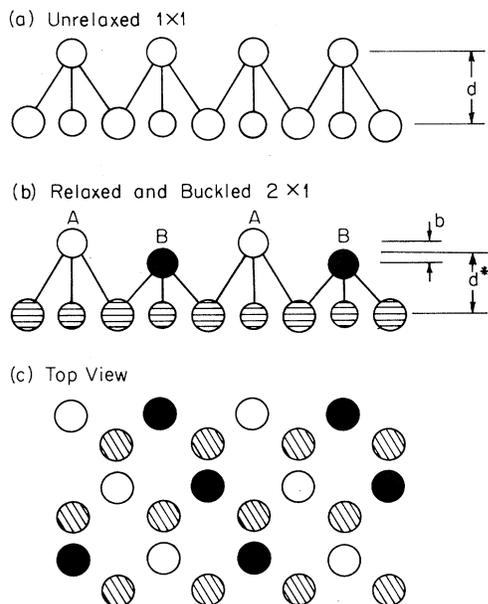
(c) Top View

FIG. 2. (a) Schematic representation of the ideal unrelaxed Si(111) 1×1 surface showing the first two surface layers in a side view. (b) Relaxation and buckling according to Haneman's model viewed from the side. (c) Top view of the relaxed and buckled surface showing rows of raised (A) and lowered (B) atoms in the surface layer.

On buckling of the surface plane the bonds dehybridize and charge is transferred from atom B which moves towards the bulk to atom A which projects from the surface. Energy-minimization calculations by Chadi[10] indicate that the charge transfer which accompanies the buckling is the dominant effect, the net charge transfer being of the order of 0.25–0.3 electron. Only a small charge transfer of less than 0.04 electron is associated with the inward relaxation of the surface plane.[10]

The charge transfer implied by the theoretical studies is in good agreement with our findings for the clean surface. For a Si surface atom which is more electropositive (electronegative) than a bulk Si atom a chemical shift towards higher (lower) binding energy will result. This is clearly evident from Fig. 1(b) where a shift to higher binding energy is observed for those Si surface atoms which have donated electrons to the chemisorbed oxygen atoms. The buckling results in a binding energy shift to lower values for atoms A (increased charge density) and to higher values for atoms B (decreased charge density). Experimentally we find two core-level components S_1 and S_2 shifted by −0.6 eV to lower and +0.3 eV to higher binding energy. These are thus interpretated as belonging to Si atoms A and B in the surface layer, respectively. To estimate the expected core-level shift due to a change in valence charge, we use a simple electrostatic model which assumes that the effect of valence charge transfer on the core-level binding energy is the same as the effect of core-electron–charge transfer on the valence band. The effect on the valence band due to one less electron in the core is the same as the effect due to one more proton in the nucleus. Therefore, a good approximation of the core-level energy shift due to the loss of one valence electron is the change in the hybird energy between Al, Si, and P.[17] This energy changes by an average of 2.1 eV between Al, Si, and P,[17] thus implying a core-level shift of 2.1 eV per Si valence electron. For a charge transfer of 0.25 electron from atoms B to A this would suggest a core-level shift of ±0.5 eV.

It is tempting to decompose the observed shifts of +0.3 and −0.6 eV into a ±0.45-eV shift due to charge transfer upon buckling and a −0.15-eV center-of-gravity shift due to relaxation of the surface layer relative to the bulk. However, it appears from present calculations[10] that the charge transfer upon relaxation is too small to account for a −0.15-eV shift. Besides the absolute value

of the charge transfer upon buckling the nonspherical charge distribution of the valence electrons at the surface will affect the chemical shift. The nature and geometry of the bond to the second layer is found[10,12] to be quite different for atoms A and B. This will modify the shifts expected from a pure charge-transfer model. An estimate of this effect is, however, quite difficult without a detailed theoretical calculation. It is interesting to note that the observed broadening of the surface peaks S_1 in Fig. 1 appears to be explainable by energy minimization calculations of Chadi.[10] He finds a well-defined energy minimum for the position of atom B while the outward motion of atom A is less well defined energetically.

The derived ratio of the surface to bulk photoemission intensity for the clean surface I_S/I_B = 0.57 can be used to derive a mean electron scattering length λ.[5] Using the known spacings between the Si layers and an average acceptance angle of $48°$ for the CMA with respect to the Si surface, we obtain $\lambda = 4.1 \pm 0.3$ Å at $h\nu = 150$ eV, in good accord with published values.[18]

The surface structures S_1 and S_2 disappear upon small oxygen exposures indicating "healing" of the cleaved reconstructed surface. Even for submonolayer coverage of oxygen charge neutralization of the previously polar surface appears to be achieved. The chemical shift of 0.9 eV for the oxygen-exposed surface is *smaller* than those previously reported.[18] We attribute the doublet O in Fig. 1(b) to Si atoms which are bonded to oxygen in form of O_2 or more likely[19] OH molecules on the surface. We believe that this chemisorption state is the same as the one discussed before by Garner *et al.*[20] These authors, however, did not find a chemical shift of the Si $2p$ level, which we attribute to the poor experimental resolution of their core-level spectra.[20]

Previously Eberhardt *et al.*[21] performed high-resolution studies of the $2p$ core levels for a series of *in situ* cleaved Si samples as a function of doping. For the sample which exhibited a doping $(n = 10^{14}$ cm$^{-3})$ closest to the one used in the present study a line broadening was observed when the photon energy was increased from threshold (~100 eV) to 150 eV. At 150 eV their instrumental resolution was comparable to ours. The line broadening was attributed to fluctuations in the chemical shifts of Si atoms in the first few surface layers which become more apparent at higher photon energies because of an increasing surface sensitivity (decreasing escape depth). Unfortunately the surface orientation of their samples was not specified by Eberhardt *et al.*[21] If we assume that they were polymorphic, a broadening due to a distribution of surface shifts is indeed plausible. This would also lend additional credibility to our earlier conclusion that the surface structures S_1 and S_2 observed by us are characteristic for the Si(111) 2×1 surface. It appears that our experimental results for the core-level shifts at the Si(111) 2×1 surface can now serve as a test criterion for a complete theoretical description of the reconstruction.

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Mechanical Shear of Layers in Smectic-A and Smectic-B Liquid Crystal

M. Cagnon and G. Durand

Laboratoire de Physique des Solides, Université de Paris-Sud, F-91405 Orsay, France

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The force transmitted through the layers of smectic-A and smectic-B phases of butyloxy-benzylidene-octylanine (4O.8) have been measured at frequencies between 1 and 10 000 Hz, in the presence of an ac shear parallel to the layers. It is found that the smectic-A behaves as a viscous fluid. The smectic-B shows an elastic response, with a shear modulus $C_{44} \sim 10^6$ cgs units. The low-frequency plastic behavior and the high-frequency dispersion which is related to internal friction are discussed.

Smectic liquid crystals are layered systems. Lower symmetry smectic phases, like the S_B, show a regular molecular ordering inside the layers, although higher symmetry ones, like the S_A, are considered as liquidlike inside the layers. Contrary to three-dimensional (3D) crystals, the smectic phases are defined through the ability of their layers to glide easily on top of each other. An important question is: Should smectic-B liquid crystals be considered true liquid crystals or 3D solids? Different models[1] have been proposed for the B phase, considered for instance[2] as a piling of two-dimensional crystals, with possible hexatic[3] order. Recent x-ray experiments on thin films[4] or in bulk[5] smectic-B samples demonstrate that on a 1 μm (or more) scale, the smectic-B appears as a 3D solid. Closer to the above accepted definition, mechanical experiments with use of ultrasonic techniques have been designed to observe the shear of the smectic layers on top of each other. The results indicated the existence of an elastic response to the shear, with an elastic modulus in the range of 10^8 cgs[6,7] or lower than 10^7 cgs.[8] However, all these results were obtained in the megahertz frequency range, too high to give definite conclusions in the presence of relaxation processes. We present here the first mechanical experiment in the very low-frequency range (down to 1 Hz), to test if the response of a smectic-B liquid crystal to a shear parallel to the layers is elastic or viscous.

Our experimental setup is very similar to the one already described[9] with the only difference being that we use shear strains and stresses, instead of compression. The sample is butyloxy-benzylidene-octylanine (4O.8) which undergoes the following transitions:

$$C \xrightarrow{33°C} S_B \xrightarrow{49.5°C} S_A \xrightarrow{63.7°C} N \xrightarrow{79°C} I.$$

The sample is oriented homeotropically with use of a silane surface treatment of the two boundary glass plates (see inset of Fig. 1). The glass plates are cemented to a piezoelectric ceramic which is in turn cemented on a rigid holder, placed inside an oven and regulated to ± 0.05 °C. The ceramic is so polarized as to create a displacement δ parallel to the layers, when applying an electric field as shown in Fig. 1. Optical inspection is possible for the central region. The parallelism of the two glass plates can be trimmed with three adjustable spacers and screws, to within $\pm 10^{-4}$ rad. The thickness can be adjusted from 30 to 200 μm. The sample available surface is a 5×12 mm^2 rectangle. The upper ceramic is driven by an ac voltage $V_i \times \exp(i\omega t)$ (in the range of 10–100 V, from 0.1 to 10 kHz) to induce an ac shear strain parallel to the layers. The lower ceramic, submitted to the transmitted shear stress, gives an output voltage $V_0 \exp i(\omega t + \varphi)$ (in the range of 100–1000 μV). The

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