

## Evidence for Site-Sensitive Screening of Core Holes at the Si and Ge (001) Surface

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Typically surface core-level shifts (SCLS) of clean surfaces are explained in the initial-state model, thus ignoring the screening of the photon-induced hole. We will show that this approach is not valid for the (001) surfaces of Si and Ge. Using *ab initio* density-functional theory we calculate the SCLS from differences of total energies of slabs containing excited atoms at different positions at the surface and in the bulk. Comparison with initial-state results reveals an enhanced screening at the surface, which is even remarkably different for the two atoms forming the surface dimer.

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X-ray photoemission spectroscopy is a widely applied and valuable tool for surface analysis. Such studies provide information about both the electronic structure at the surface (e.g., details concerning the bonding of surface atoms or adsorbates) and the surface atomic geometry. In the photoabsorption process the photon energy is transferred to a core electron, which thereby obtains an energy above the vacuum level and can be measured as a photoelectron. The surface core-level shift [1] (SCLS) is defined as the difference in kinetic energy of an electron that has been emitted from a surface atom compared to one originating from a bulk atom. Usually, SCLS are interpreted in terms of the initial-state picture: The single-particle energy eigenvalue of a core state which is localized at a surface atom in general differs from that of a bulk atom due to the different chemical environments, and in the initial-state picture it is assumed that this difference equals the SCLS. What is omitted in this model is the response of the valence electrons to the creation of the core hole [2,3], and the possibility that this response may be different at the surface and in the bulk. In a real solid the photocreated core hole will be screened, and if this screening happens sufficiently fast, the screening energy will be transferred to the photoelectron, which therefore appears at a higher kinetic energy.

Usually it is assumed that the screening at surfaces and in the bulk is very similar. Sometimes it is argued that screening at a semiconductor surface is reduced compared to the bulk, because one half space of dielectric material is missing [4]. However, in this paper we will show that for Si(001) and Ge(001) the opposite is true, namely, that final-state relaxation plays a crucial role for the SCLS, and that screening is in fact enhanced at the surface. Moreover, looking at the surface geometry one would expect that screening should be very similar for all top-layer surface atoms. Again this assumption is incorrect. The key to understanding the mechanism behind these peculiar screening properties is found in the surface electronic structure, as will be explained below. Although the effect has not been discussed so far we argue that it should be active on many other semiconductor surfaces as well.

The geometric structure of the (001) surface of silicon

and germanium [5] is sketched in Fig. 1. Especially in the case of the silicon surface, there was a long-lasting discussion [6,7] whether the dimer bond is parallel to the surface or not. However, recent density-functional calculations [8,9] and low-temperature scanning tunneling microscopy results by Wolkow [10] provided convincing evidence that dimers are in fact buckled.

The most important feature of the structure depicted in Fig. 1 is the existence of two inequivalent positions for the dimer atoms. In the following we will denote the atom which is displaced towards the vacuum region as the "up" atom, and the atom nearer to the bulk as the "down" atom. These two inequivalent positions are expected to show up in the core-level photoemission spectra as two separate peaks. Unfortunately, limited resolution has often complicated the interpretation of experimental spectra. Moreover, the correct assignment of observed photoemission peaks to atomic sites has also been a matter of intense recent dispute [7,11,12].

In the case of Si(001), well resolved Si  $2p$  core-level spectra by Landemark *et al.* [13] are now available, which have helped to clarify the situation (see bottom panel of Fig. 2). Emission from the up atom is found at a kinetic energy of +0.49 eV above the bulk peak. The emission from the down atom almost overlaps with the bulk emission; it is located at -0.06 eV (i.e., at lower kinetic energy than photoelectrons from the bulk). Furthermore there are photoelectrons with even lower kinetic energy at -0.22 eV below the bulk peak. They are not to be assigned to any surface dimer atom (as had been suggested in some older work), but it is argued that they originate

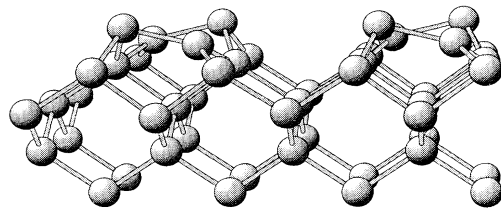


FIG. 1. Atomic structure of the  $p(2 \times 2)$ -reconstructed (001) surface of Si and Ge. The buckling angle alternates along the dimer rows.

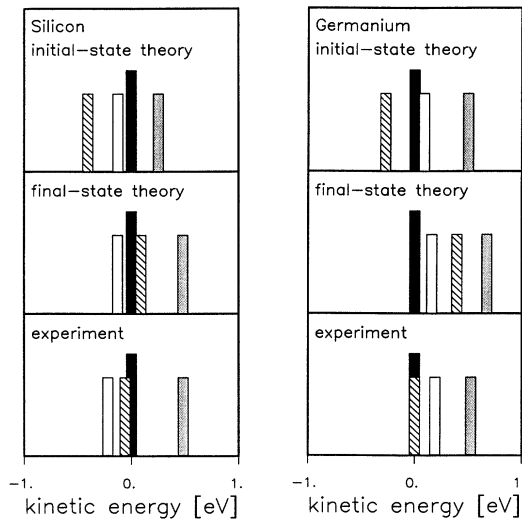


FIG. 2. SCLS for the Si(001)- $p(2 \times 2)$  (left panel) and Ge(001)- $p(2 \times 2)$  (right panel) surface. The kinetic energy (relative to bulk emission, which is denoted by a black bar) of the photoemission maxima is indicated by different bars. The gray, hatched, and white bars correspond to emission from up, down, and second-layer atoms, respectively. Top: results from initial-state theory. Middle: results from full theory, including core-hole screening. Bottom: experimental results from Landemark *et al.* [13,16].

from the second layer.

For the Ge(001) surface the experimental findings are less clear, because all available Ge 3*d* core-level spectra are less well resolved than Landemark's Si 2*p* spectra. The only structure that is easily visible in all photoemission spectra is a shoulder at about +0.5 eV kinetic energy, which is attributed to emission from the Ge up atoms. From intensity variations in photoemission spectra following adsorption experiments Ranke and co-workers [14] have concluded that, besides the emission from the up atom at +0.45 eV, there is a contribution from the down atoms which is overlapping with bulk emission within  $\approx \pm 0.1$  eV. Besides the shoulder at +0.54 eV, Cao *et al.* [15] found another photoemission peak at +0.19 eV. From their epitaxy experiments the authors conclude that this peak is not due to top-layer dimer atoms, but to subsurface emission. Recently Landemark [16] got similar values for the SCLS, i.e., +0.52 eV for the up atom and +0.19 eV for the second-layer atoms.

Initial-state SCLS for the Si and Ge(001)- $p(2 \times 2)$  surfaces have been calculated by Dąbrowski *et al.* [17] using density-functional theory (DFT) together with the local-density approximation (LDA) for the exchange-correlation functional (see top panel of Fig. 2). The effective potential is extracted from a ground-state calculation of a  $2 \times 2 \times 12$  slab, and averaged within spheres centered around the atomic positions. Differences of this averaged potential between different atoms reflect differ-

ences in core-level single-particle binding energies of the respective atoms. Theoretical values of the SCLS for Si (Ge) are +0.25 eV (+0.50 eV) for the up atom, -0.41 eV (-0.27 eV) for the down atom, and -0.13 eV (+0.09 eV) for second-layer atoms [18]. The physical picture that has emerged from these calculations is that the surface atoms are immersed in a background potential which is increasing towards the vacuum. Therefore, the dimer atom displaced towards the vacuum region is energetically shifted upwards, leading to a positive SCLS [17]. A serious shortcoming of initial-state theory becomes apparent: It predicts the photoemission peaks with highest and lowest kinetic energy to be due to top-layer up and down atoms, respectively. Emission from second and deeper layers only results in photoemission peaks closer to the bulk peak, surrounded by the up and down peak. On the other hand, for Si in experiment the down-atom derived peak almost overlaps with bulk emission, and the maximum in the Si 2*p* photoemission spectrum at low kinetic energy is in fact due to second-layer atoms. Therefore, an assignment of photoemission peaks to atomic positions based on this simple model would be incorrect. Similarly, also in the case of germanium, the emission from the down atom is predicted at a distinctly too low kinetic energy. This unsatisfying comparison between initial-state theory and experiment has led us to investigate the role of screening at these surfaces.

In the photoemission experiment the initial state consists of a crystal in its ground state plus a photon, and the final state is a crystal with a core hole plus a photoelectron. Therefore, in the case of static screening, the SCLS is given by total-energy differences of crystals containing a core hole at different positions. Under typical experimental conditions the Fermi level is fixed by dopants. The Fermi level acts as a reservoir of electrons, which implies that the crystal containing a single core hole can be treated as neutral.

The mentioned total-energy differences are calculated [19] within DFT-LDA, using an 8- (Si) or 12- (Ge) layer slab with a  $(2 \times 2)$  surface unit cell. We generated Hamann-Schlüter-Chiang [20] type norm-conserving pseudopotentials for Si and Ge, and Si and Ge atoms with a screened 2*p* or 3*d* core hole, respectively (i.e., the occupation of the core level is decreased by one, and the number of the outermost *p* electrons is increased by one). In this way our calculations are more accurate than the well-known " $Z + 1$ " impurity model [1], because we do not approximate the core hole by a point charge centered at the atomic nucleus [21]. Lattice constants (10.16 bohrs for Si and 10.57 bohrs for Ge) and relaxed atomic coordinates have been taken from Dąbrowski and Scheffler [9]. An energy cutoff of 12 Ry (Si) and 8 Ry (Ge) for the plane-wave basis set of the Car-Parrinello-like program and 16 *k* points in the full two-dimensional Brillouin zone [22] proved to yield sufficiently accurate results (convergence error less than 30 meV). We also made an attempt to correct our results for core-hole interaction (which is a

disadvantage inherent to any supercell method) using a simple electrostatic model with point charges immersed in the dielectric of a capacitor. The conducting plates simulate the screening by electrons in surface states. The main result is a larger interaction energy for bulk core holes ( $< 0.15$  eV) than for core holes near the surface. As peak splittings at the surface are very little affected, this correction does not affect the conclusions in this paper. Doing a calculation for a Si ( $4\times 4$ ) cell at 8 Ry cutoff energy we obtained that the energy splitting between the up and down atoms is changed only little (30 meV) compared to a calculation for a ( $2\times 2$ ) cell. This shows that the SCLS results as obtained from the small ( $2\times 2$ ) cell are reliable.

Results from the full final-state theory are summarized in Fig. 2 (middle panel); the SCLS for Si (Ge) are +0.48 eV (+0.67 eV) for the up atom, +0.09 eV (+0.39 eV) for the down atom, and  $-0.13$  eV (+0.16 eV) for second-layer atoms. The position of bulk emission (which is used as a reference) has been estimated by averaging the kinetic energies of photoelectrons that originate from the innermost layers of the slab. Because the core-level binding energies still differ for the innermost layers of the 8-layer Si slab, there is an uncertainty in the position of the bulk emission of about 0.1 eV. The relaxation energy, which results from the response of the valence electrons to the core hole, is obtained from the difference between initial- and final-state results. We observe an enhanced screening at the surface, and that core holes in subsurface atoms below the surface dimers are better screened than core holes near the valley between dimer rows. In particular, the gain in relaxation energy is largest when the core hole is created in the down atom of the dimer. The SCLS from the full theory differ considerably from those based on the simple initial-state theory, and the comparison with experiment is improved by inclusion of final-state effects: In the case of Si the peak with lowest kinetic energy is now really due to emission from subsurface (second-layer) atoms. Also in the case of Ge the down-atom peak is shifted above the bulk peak. However, for Ge screening seems to be overestimated by our calculations; a possible reason for this might be that screening of the core hole is imperfect, as the dynamics of screening comes into play. In this case one would expect emission in the energy range between the initial-state result (no screening) and our final-state result (complete, static screening).

The unexpectedly large relaxation shift for core-level photoelectrons emitted from the down atom can be explained within a simple physical picture, somewhat analogous to the behavior known for atoms and molecules chemisorbed on metals [23,24]. Both for Si(001) and Ge(001) there are two surface-state bands in the fundamental gap [25,26] (see Fig. 3): The occupied band corresponds to dangling bonds which are localized at the up atom, while the second surface-state band is unoccu-

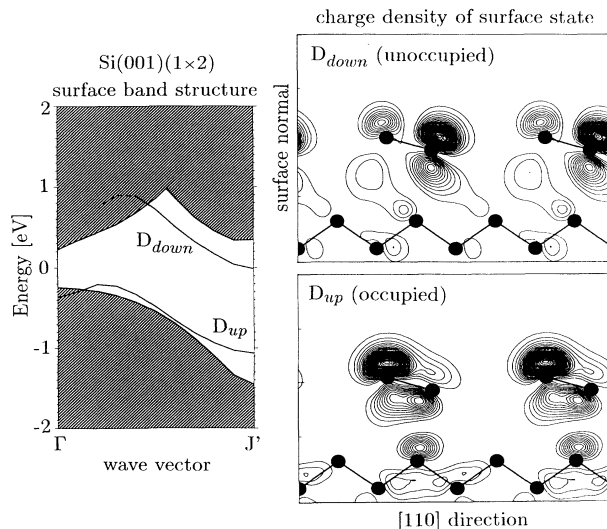


FIG. 3. Left: Surface band structure (from DFT-LDA eigenvalues) of the Si(001)-(1 $\times$ 2) surface. There are two surface bands, an occupied band with dangling-bond states located at the up atom ( $D_{up}$ ), and an unoccupied band with dangling-bond states located at the down atom ( $D_{down}$ ). Right: charge density of two wave functions typical for the  $D_{up}$  and  $D_{down}$  band.

ried, with the wave functions being localized at the down atom. If a core hole is created in the down atom, the induced potential pulls down the unoccupied dangling-bond state, which then becomes occupied by electrons from the Fermi level. Because of the localization of the involved orbital this leads to a very efficient screening of the core hole. This mechanism expresses itself in the induced charge densities. Always, most of the screening charge is localized at the respective atom. In order to focus on the differences between the screening of core holes at different sites, the spherical screening pseudo-charge-density of an isolated atom (with a Ge 3d electron excited into the 4p level) has been subtracted. This difference is displayed in Fig. 4 for core holes in an up or down atom. When the core hole is located in the down atom, the charge-density difference resembles the charge density of the dangling-bond state localized at this atom.

In conclusion, we have demonstrated that final-state effects are essential for understanding core-level photoemission spectra from the (001) surfaces of Si and Ge. The physical mechanism is traced back to the surface electronic structure; an empty dangling-bond state localized at the down atom is pulled down and becomes occupied. We expect that this mechanism should also be relevant for other semiconductor surfaces, provided that the surface band gap is small and that there exist unoccupied states with localized wave functions.

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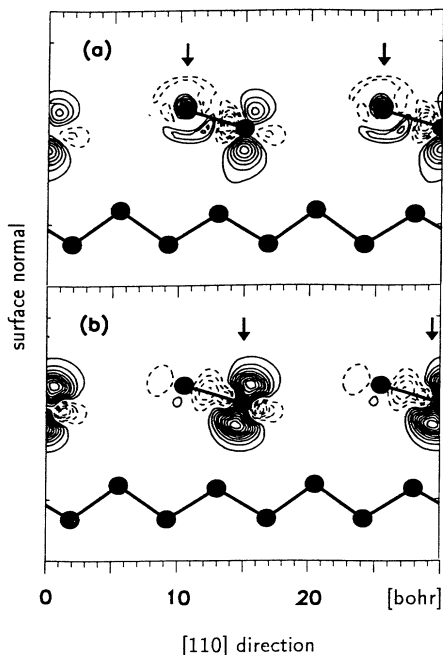


FIG. 4. Screening charge density minus spherical "screening" charge density for a single excited atom (see text) for core holes localized at an up atom (a) or a down atom (b). Full lines denote an increase of electron density; dashed lines a decrease. The contour levels are equidistant with spacing  $\delta\rho = 0.87 \times 10^{-3}$  electrons/bohr<sup>3</sup>. The positions of core holes are denoted by arrows. Results are from a 12-layer Ge(001)-(2 × 2) supercell calculation.

concerning experimental aspects.

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