

Absolute Determination of Surface Core-Level Emission for Ge(100)-(2×1) and Ge(111)-c(2×8): Surface Reconstruction and Defects

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The number of surface atoms on Ge(100)-(2×1) and Ge(111)-c(2×8) which contribute to the Ge 3*d* core shift is determined by a combination of synchrotron photoemission, high-energy electron diffraction, and molecular-beam epitaxy techniques. The result is 0.87 ± 0.09 monolayer for Ge(100)-(2×1), revealing that the buckled-dimer bond is primarily covalent in nature. The Ge(111)-c(2×8) surface shows "adatom" emission corresponding to 0.33 ± 0.04 monolayer; the departure from the ideal value of 0.5 monolayer is attributed to a large number of defects on the surface.

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We present a novel application of synchrotron photoemission, high-energy electron diffraction (HEED), and molecular-beam epitaxy (MBE) to a precision determination of the number of surface atoms of a semiconductor crystal which contribute to the surface core-level binding-energy shift. Surface core-level shifts as measured by photoemission have been observed for a variety of systems, and are a consequence of the different bonding environment at the surface relative to the bulk.^{1,2} A precision quantification of the shift can provide information concerning the local chemical environment of surface sites, and is paramount for an elucidation of the interplay between specific features of the reconstruction and surface electronic properties in general. The photoemission intensities of the surface-shifted core-level peaks reflect the relative population of each surface site, and much of the quantitative work in core-level spectroscopy has been concerned with the determination of the absolute population of surface sites. This is especially important for semiconductor surfaces which often show complex reconstructions with several inequivalent surface sites. In addition, because of the presence of intrinsic surface defects, the absolute population of each site is not necessarily a simple fraction of a monolayer. Previously, core-level spectroscopy analysis of the intensity has relied heavily on the phenomenological electron escape depth which is generally uncertain and depends sensitively on the sample-to-analyzer collection geometry.^{1,2}

The systems under study are the technologically relevant Ge(100)-(2×1) and Ge(111)-c(2×8) surfaces, which have previously received considerable experimental and theoretical attention. As a result of uncertainties in the electron escape depth, different photoemission studies of the Ge surfaces have led to large discrepancies in reports for the number of surface atoms giving rise to the core shifts. In particular, results for Ge(100) have ranged from about 0.6 to 1 full atomic layer; the discrepancy has led to very different interpretations of the nature of the (2×1) reconstruction.^{1,3-5} The basic

structural unit on Ge(100)-(2×1) is the buckled dimer, as confirmed by a recent scanning tunneling microscopy (STM) study.⁶ It has been proposed that the buckling is associated with charge transfer between the two atoms in a dimer,⁷ and results in an ionic bond between the two atoms with bonding configurations of s^2p^3 and sp^2 .⁸ Yet it has also been pointed out that a large charge transfer is unlikely because of the strong intra-atomic repulsion.^{9,10} Since any charge transfer would cause the local electrostatic potential to shift, leading to a corresponding core-level binding-energy shift,¹ a clarification of the surface emission intensity is necessary for an evaluation of the symmetry of the valence charge distribution about the buckled-dimer atoms; this work also has important ramifications concerning the similar Si(100)-(2×1) surface. For the Ge(111)-c(2×8) surface, STM results reveal the presence of fairly small domains exhibiting several reconstructions.¹¹ We will see below that the resulting defects associated with the domain structure cause the surface core-level emission to depart significantly from a simple ideal fraction of a monolayer. The present work also intends to establish a coherent basis for future quantitative core-level studies of the adsorbate chemistry and interface formation on these surfaces.^{1,12}

The present experimental approach is free from the employment of an estimated escape depth, and represents a direct measurement of surface coverages. This ability is extremely important for many areas of surface studies. For instance, the recent controversy about the structure of $(\sqrt{3} \times \sqrt{3})$ Ag overlayer on Si involves an uncertainty in the absolute Ag coverage.¹³ In order to determine the number of surface atoms which contribute to the Ge 3*d* core shifted peaks for the Ge(100)-(2×1) and Ge(111)-c(2×8) surfaces, a reference sample of Si(100)-(2×1) deposited with 0.25 monolayer (ML; 1 ML = 6.24×10^{14} atoms/cm²) of Ge is prepared so that when it is placed in the same sample-to-analyzer collection geometry as a Ge surface, the Ge 3*d* core emission

from the reference provides an absolute intensity calibration. Thus, the number of surface atoms contributing to each shifted core-level peak on the Ge surfaces is obtained by direct comparison with the reference sample.

In our experiment, the Ge deposition was done by evaporation from an electron-beam-heated tungsten crucible. The absolute evaporation rate was determined by measurement of the period of the HEED intensity oscillations during the MBE growth of Ge on Ge(100)-(2×1). Figure 1 shows a typical trace of HEED intensity of the specularly reflected beam along the [010] azimuth as a function of evaporation time. The HEED intensity oscillation is a well-established effect, where the period of oscillation corresponds to the growth of exactly 1 monolayer.¹⁴⁻¹⁶ Once the absolute rate was calibrated, the reference sample of Si(100) covered with 0.25 ML of Ge was prepared by timed evaporation onto a freshly cleaned Si(100)-(2×1) substrate. The Si(100) substrate temperature was maintained between 200°C and 300°C during the evaporation of Ge. The growth of Ge on Si(100) is layer by layer with no apparent intermixing for the first few atomic layers in this temperature range,^{17,18} allowing for the preparation of an unattenuated submonolayer reference.

The clean Ge(100) and Ge(111) surfaces with ordered reconstructions were obtained by repeated cycles of sputtering and annealing to 600°C for the Ge(100) surface and 800°C for the Ge(111) surface. For the Ge(111) surface, distinct eighth-order spots with a low background indicative of a well-ordered $c(2\times 8)$ reconstruction were observed. For the Ge(100) surface, a small mixture of quarter-order and half-order spots indicative of some $c(4\times 2)$ and (2×2) ordering was observed

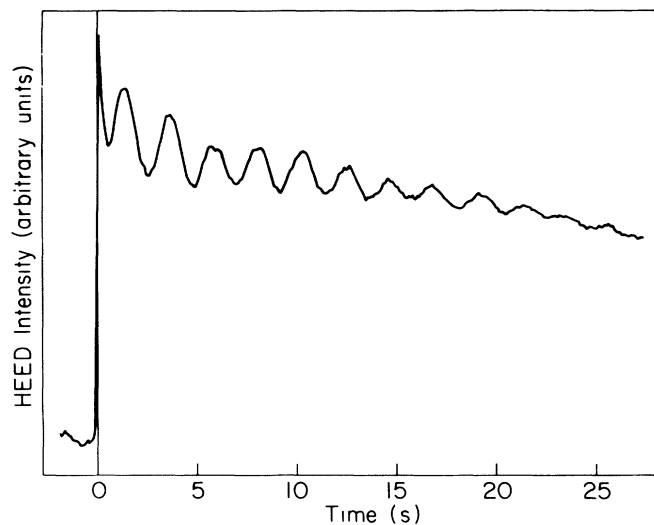


FIG. 1. HEED intensity oscillations during the MBE growth of Ge(100). The intensity of the specularly reflected spot along the [010] azimuth as a function of time during growth is shown.

within a sharp (2×1) pattern. It is the intensity of the (2×1) and $c(2\times 8)$ patterns which suggests the nominal Ge(100)-(2×1) and Ge(111)- $c(2\times 8)$ conventions used here.

The photoemission experiments were carried out with synchrotron radiation from the University of Illinois beam line on the 1-GeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin-Madison. Light from the ring was dispersed by an extended-range grasshopper monochromator, which was designed and constructed by F. C. Brown and his co-workers. The photon flux was monitored by measurement of the photocurrent from a gold-wire screen situated before the samples. The photoelectrons were analyzed with a large hemispherical electrostatic analyzer. The overall instrumental resolution was about 0.2 eV. The photoemission, HEED, and MBE experiments were all performed in the same vacuum chamber. All samples for photoemission were positioned in the same sample-to-analyzer collection geometry such that the intensities from different samples can be directly compared.

Typical surface-sensitive photoemission spectra from the Ge 3*d* core level taken with a photon energy of 90 eV for Ge(111)- $c(2\times 8)$ and Ge(100)-(2×1) are shown in Fig. 2. The corresponding bulk-sensitive spectra are not shown here and can be found in earlier publications.^{3,4,19,20} By comparing spectra with varying surface sensitivities, these previous studies employing a nonlinear

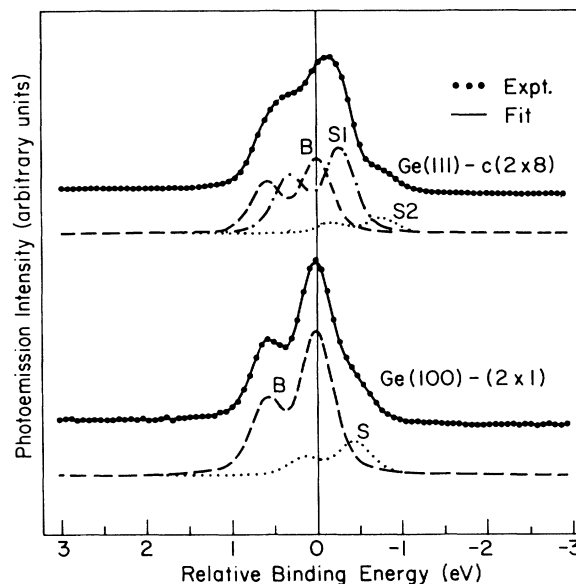


FIG. 2. Ge 3*d* core-level spectra taken with a photon energy of 90 eV for the Ge(111)- $c(2\times 8)$ and Ge(100)-(2×1) surfaces. The solid curves running through the data points (dots) are the fits to the data. The other curves show the decomposition of the spectra into bulk (*B*) and surface (*S*, *S*₁, and *S*₂) contributions. The binding energy is referred to the bulk Ge 3*d*_{5/2} components.

least-squares fitting procedure have shown that the line shapes contain surface and bulk contributions. The decomposition into various components as well as the overall fit to the line shape is indicated in Fig. 2 by the various curves. The Ge(100)-(2×1) surface shows a surface component (labeled *S* in the figure) shifted by 0.43 eV relative to the bulk component (labeled *B*), while the spectrum for the Ge(111)-*c*(2×8) shows two surface components, *S*1 and *S*2, shifted by 0.27 and 0.77 eV, respectively, relative to the bulk component. The details of the line-shape analysis and the basis for assignment of the various peaks can be found in previous publications and will not be repeated here.^{3,4,19,20} In all cases, each component exhibits a spin-orbit splitting of 0.59 eV.

In order to assess the statistical average and uncertainty for the measured number of surface atoms contributing to the core shift, the experiment and analysis were repeated for many independent preparations of the Ge(100)-(2×1), Ge(111)-*c*(2×8), and Ge-on-Si(100) reference samples. The same results were consistently reproduced within close tolerances. From the fits to the spectra, the weights (fraction of total intensity) of the *S*, *S*1, and *S*2 components are 0.192, 0.488, and 0.084, respectively. By comparison of the core emission intensities of the Ge reference samples and that from the *S* component of Ge(100)-(2×1), the average number of Ge(100)-(2×1) surface atoms which contribute to the *S* emission is 0.87 ± 0.09 ML, where the error bar represents two standard deviations of the many data points obtained.

From the STM images of Ge(100)-(2×1), most of the surface consists of buckled dimers with some defects in the form of missing dimers within a given (2×1) domain, and missing dimer pairs exist along certain monatomic stepped boundaries which separate two orthogonally oriented domains.⁶ An inspection of the limited-area STM topographs indicates that roughly 5%–10% of the surface suffers from such defects. Thus, a nearly full monolayer contribution to the *S* emission indicates that both the “up” and “down” atoms in a buckled dimer contribute to the core shift. The (0.13 ± 0.09)-ML deviation in the *S* emission from the ideal fully dimerized surface is consistent with the density of missing-dimer defects estimated from the STM study. Furthermore, it is possible that the measured density of missing-dimer defects depends on the particular sample preparation technique which may in part explain the discrepancy between the present result and the value of 0.62 ± 0.05 ML contributing to the *S* emission reported by Schnell *et al.*⁵

The apparently equivalent contribution of both atoms in a buckled dimer to the *S* emission has immediate implications concerning the symmetry of the valence charge distribution about the buckled dimer. From earlier studies of chemisorption-induced shifts on Si and Ge sur-

faces, highly ionic and covalent adsorbate-to-substrate bonding is found to induce an energy shift of approximately 1 and 0.5 eV, respectively, indicating roughly a 1-eV shift per one effective electron transfer.^{1,12,21,22} Evidence for a fully ionic bond between the up and down dimer atoms on Ge(100)-(2×1) would necessitate the existence of two surface core-level components separated by about 2 eV, each corresponding to about $\frac{1}{2}$ ML. A smaller charge transfer would result in a correspondingly smaller energy separation. Final-state screening effects could cause an additional overall shift for both surface components in the same direction relative to the bulk component, possibly rendering one component indistinguishable from the bulk component.^{1,23} Thus, it is very important to determine whether the *S* emission corresponds to about 1 or $\frac{1}{2}$ ML (namely, both kinds of dimer atoms or just the up atoms). Our experimental finding of nearly 1-ML contribution to the *S* emission clearly rules out any significant charge transfer. Thus, within the confines of our experimental resolution for this core-level deconvolution procedure, the buckled-dimer bond appears to be mainly covalent in nature; the charge transfer between dimer atoms is estimated to be no more than about 0.1*e*. In a different but related experiment, the authors found a value of 0.92 ± 0.07 ML contributing to the *S* emission for the very similar Si(100)-(2×1) surface, and concluded that the dimer bond on Si(100)-(2×1) is also mainly covalent in nature.²⁴

Previously, the *S*2 and *S*1 components of the Ge(111)-*c*(2×8) core line shape have been identified as emission from the adatoms and first full double layer beneath the adatoms.¹⁹ From the present study, the average *S*2 and *S*1 emission corresponds to 0.33 ± 0.04 and 1.9 ± 0.2 ML, respectively, where 1 ML here represents a Ge(111) atomic layer (7.2×10^{14} atoms/cm²). The limited-area STM topographs of the Ge(111)-*c*(2×8) surface show reconstructions of *c*(4×2), (2×2), and *c*(2×8) in very small domains.¹¹ The surface exhibits protrusions with a density of roughly 0.45 ML, with 10% of the surface exhibiting missing protrusions. It is conceivable that the protrusions represent adatoms, similar to the case of Si(111)-(7×7) where the protrusions in the STM images correlate well with the adatoms predicted in the Takayanagi dimer-adatom-stacking-fault model of the (7×7) surface.²⁵ The difference between the observed 0.33 ± 0.04 ML and the ideal 0.5 ML for the adatom density of a perfect *c*(2×8) structure is apparently due to the defects; the discrepancy with respect to the STM value is probably due to a significantly larger number of defects from sampling over a large macroscopic region compared to the limited region scanned in the STM study.

In summary, we have demonstrated a technique of general utility to quantify precisely the surface core-level emission. For Ge(100)-(2×1), the result is that 0.87

± 0.09 ML contributes to the surface core-level shift, precluding large asymmetrical charge distributions about the buckled dimer. For Ge(111)- $c(2\times 8)$, a large adatom defect density is observed. The ability to prepare an absolute coverage or intensity reference is extremely important for many areas of surface and interface studies.

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