

Surface core-level shifts for clean and halogen-covered Ge(100) and Ge(111)

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The intensity and energy shift of the Ge 3*d* surface core-level photoemission is determined with the use of synchrotron radiation. Cl- and Br-terminated Ge(111)-(1×1) surfaces are used to calibrate the absolute coverage Θ and to obtain accurate line shapes. We find binding-energy shifts $\Delta E = +0.57$ eV for Cl/Ge(111)-(1×1) and for Cl/Ge(100)-(2×1), $\Delta E = +0.47$ eV for Br/Ge(111)-(1×1), $\Delta E_1 = -0.26$ eV and $\Delta E_2 = -0.76$ eV for clean Ge(111)-*c*(2×8), and $\Delta E = -0.43$ eV for clean Ge(100)-*c*(4×2). The coverage of special surface atoms (in monolayers) is $\Theta_1 = 0.93$, $\Theta_2 = 0.25$ for clean Ge(111)-*c*(2×8), $\Theta = 0.62$ for clean Ge(100)-*c*(4×2), and $\Theta = 1.03$ for Cl/Ge(100)-(2×1). The electron mean free path is 5.4 Å at a kinetic energy of 25 eV. With regard to structural models we conclude that the asymmetric dimer model fits the Ge(100) data best, with a possible contribution of 24% symmetric dimers. For Ge(111)-*c*(2×8) two new models are proposed with adatoms and tetramer building blocks, respectively.

I. INTRODUCTION

Photoemission from shifted core levels at surfaces has been observed for a variety of semiconductor and metal surfaces.^{1,2} It has been possible to obtain structural and chemical information from the intensity ratio of the surface emission relative to the bulk and from the energy shift. The energy shift provides a measure of the charge transfer to the surface atom. A simple linear relationship between charge transfer and core-level shift has been found for model compounds.³ The intensity of surface core-level emission is proportional to the coverage of chemically different surface atoms and an absolute coverage can be determined if a surface with known structure is available for calibration. Alternatively, the mean free path of the photoelectrons can be used to convert intensities into coverage via simple relations.^{4,5}

Our goal is to determine the coverage of special surface atoms with a shifted core level as accurately as possible in order to obtain structural information for Ge surfaces. Thereby we use halogen-terminated surfaces with a simple structure and large core-level shifts for calibration. We obtain two important extra pieces of information which were not available in previous work:^{4,6,7} (i) The emission intensity corresponding to a monolayer of surface atoms is measured directly for the halogen-terminated Ge(111)-(1×1) surface. Measurements on two such surfaces allow for a consistency check. (ii) The line shape of the bulk core-level peak is determined directly because the halogen adsorption removes all intrinsic surface core-level emission on the low-binding-energy side. This knowledge is particularly useful for separating surface from bulk emission and for obtaining accurate intensities.

There exist several open questions concerning the structure of Ge surfaces which can be addressed by accurate surface core-level measurements. The traditional model for Ge(100) is the dimer model.⁸ However, it is not clear whether the dimer is asymmetric or not. For Si(100), core-level measurements⁹ gave 0.5 layer of special atoms,

which indicates an asymmetric dimer. For Ge(100), a full layer of special atoms⁴ was obtained by fitting surface core-level data. Thus, the question arises whether or not there is a difference between the Ge(100) and Si(100) surface reconstruction. A recent model for Si(100) postulates a disordered surface with a certain fraction of the dimers missing.¹⁰ This model would account for a coverage of special surface atoms smaller than unity even with symmetric dimers. Another recent model for Si(100) has a full layer of chain atoms on top of dimers.¹¹

The Ge(111)-*c*(2×8) surface has a large unit cell which makes it difficult to select a structural model from the large number of conceivable models. The observation of two shifted surface core levels^{6,7} indicates a complex structure. There exist a few models based on Haneman's idea of buckling,¹² but they are unlikely in view of recent calculations¹³ which find that buckling is energetically unfavorable for homopolar semiconductors. In the wake of recent extensive work on the Si(111)-(7×7) structure, it has been proposed to arrange adatoms¹⁴ or tetramers¹⁵ into a *c*(2×8) pattern. Such models are consistent with our data in predicting 0.25 layer of special atoms on top of a full monolayer of regular surface atoms.

II. EXPERIMENTAL

The experiments were carried out at the dedicated storage ring BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung) in Berlin. The synchrotron radiation was dispersed by the toroidal-grating monochromator TGM-3.¹⁶ The photoelectrons were analyzed with an ellipsoidal-mirror display spectrometer¹⁷ operated in an angle-integrating mode. The Ge 3*d* core electrons were excited in a photon-energy range $\hbar\omega = 36$ –60 eV. The energy of $\hbar\omega = 55$ eV gave the best result with respect to the resolution of the monochromator and the surface sensitivity of core-level photoemission.

We used Ge samples with low *n*-type doping concentrations. The Ge(100) and Ge(111) surfaces were prepared

with repeated cycles of mild sputtering (600–800 eV Ar^+) and heating ($\sim 600^\circ\text{C}$). This resulted in a $c(2\times 8)$ low-energy-electron diffraction (LEED) pattern for Ge(111) and a $c(4\times 2)$ LEED pattern with elongated quarter-order spots for Ge(100).¹⁸ For the adsorption Cl and Br were produced *in situ* by dissociation of AgCl and AgBr in a solid-state electrochemical cell¹⁹ in a preparation chamber connected to the spectrometer chamber. All spectra with adsorbates presented in this paper were recorded after saturated room-temperature adsorption. Upon adsorption of Cl and Br the $c(2\times 8)$ reconstruction of the Ge(111) surface changed to a (1×1) structure. After Cl adsorption on Ge(100) the extra $c(4\times 2)$ spots vanished and a sharp (2×1) LEED pattern was seen.

III. PHOTOEMISSION RESULTS

Figure 1 shows the Ge $3d$ core-level photoemission spectra for clean and Cl-covered Ge(100) and Ge(111). Here the energy zero is taken to be the $3d_{5/2}$ bulk position, which has been determined for all four spectra in a bulk-sensitive mode with a photon energy of $\hbar\omega = 40$ eV. This eliminates the influence of band-bending changes on the binding energy.²⁰ The corresponding spectra after the subtraction of the $3d_{3/2}$ contribution and the secondary-electron background are shown in Fig. 2. The $3d_{3/2}$ stripping procedure splits the measured spectra into two equally shaped contributions ($3d_{3/2}$ and $3d_{5/2}$) and subtracts the $3d_{3/2}$ contribution. As parameters of this stripping procedure we used a spin-orbit splitting of $\Delta^{LS} = 0.585 \pm 0.01$ eV and a $3d_{3/2}$ -to- $3d_{5/2}$ branching ratio of $B = 0.58 \pm 0.02$ (0.64 ± 0.01) for Ge(111) [Ge(100)].

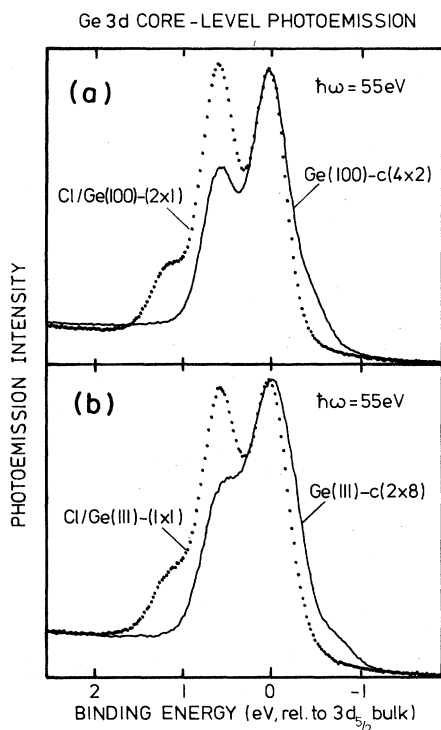


FIG. 1. Ge $3d$ core-level photoemission spectra for clean and Cl-covered Ge(100) and Ge(111) surfaces.

The difference in the B value for the two surfaces can be explained with different matrix-element effects or final-state effects.

The spectra in Figs. 1 and 2 are arbitrarily normalized at the $3d_{5/2}$ bulk peak. Already, by visual inspection of Fig. 2, we obtain various detailed information about the contribution of the shifted core level: (i) For both surfaces we see surface-related core-level emission at the low-binding-energy side of the bulk line for the clean surface. After Cl saturation adsorption surface core-level emission appears at the high-energy side. (ii) The intensity of the surface contribution on clean Ge(100) is significantly smaller than on Cl-covered Ge(100). (iii) On clean Ge(111) we can clearly distinguish, without any further assumptions, at least two surface contributions with different binding energies and intensities. (iv) The hatched area in Fig. 2(a) represents a very good approximation to the bulk line. The knowledge of the position and shape of the bulk line reduces the number of free parameters for the fits in Figs. 3–5. The intrinsic Lorentzian linewidth [190 meV full width at half maximum (FWHM)] and the Gaussian broadening due to instrumental resolution, phonon broadening, or inhomogeneities (350 meV FWHM) are obtained with this dashed area. We fitted the Ge $3d_{5/2}$ spectra in order to obtain accurate values for the energy shift and the intensity of the surface-related emission. We assume the surface components to have the same shape as the known bulk line. The free parameters for every surface component were the energy shift ΔE rel-

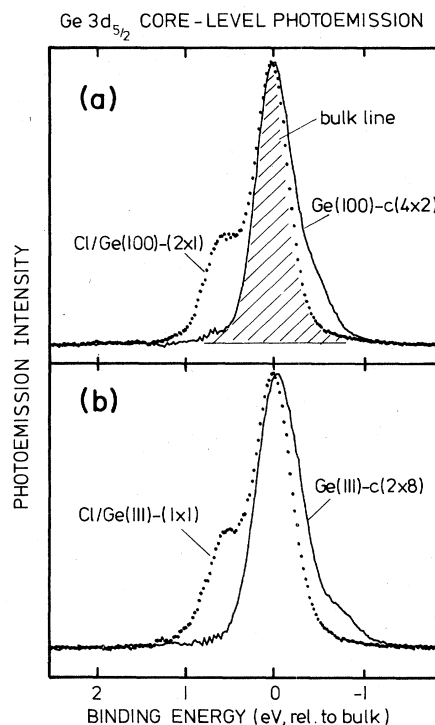


FIG. 2. Ge $3d_{5/2}$ core-level photoemission spectra for clean and Cl-covered Ge(100) and Ge(111) surfaces. Note that the intensity of the clean Ge(100) surface contribution is significantly smaller than the Cl-induced emission, indicating less than a monolayer coverage of special surface atoms.

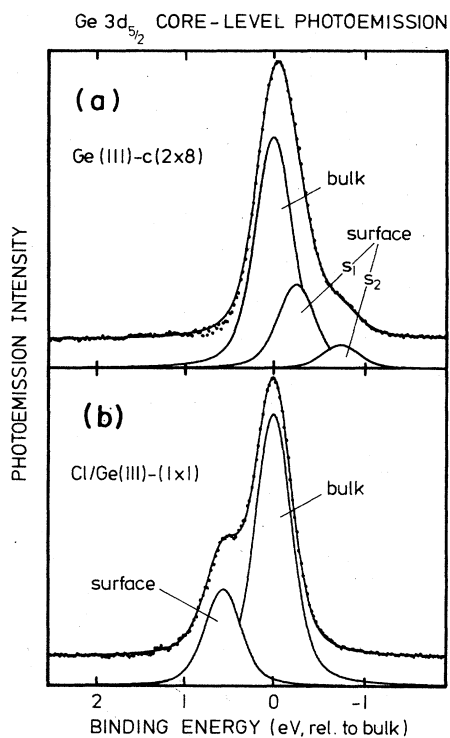


FIG. 3. Experimental and fitted Ge $3d_{5/2}$ core-level photoemission spectra for Ge(111)-c(2 \times 8) and Cl/Ge(111)-(1 \times 1).

ative to the bulk line and the intensity ratio $R = I_S / I_{tot}$ of the surface emission (I_S) relative to the total $3d_{5/2}$ emission intensity (I_{tot}). The fits for the halogen-covered surfaces [Figs. 3(b), 4, and 5(b)] and for clean Ge(100) [Fig. 5(a)] were obtained with only one surface peak. For clean Ge(111) [Fig. 3(a)] we had to introduce two surface peaks, as mentioned above. The resulting values for ΔE and R are listed in Table I.

For a discussion of surface structures it is important to know how many surface atoms (measured in monolayers) contribute to an identified shifted core-level peak. We use

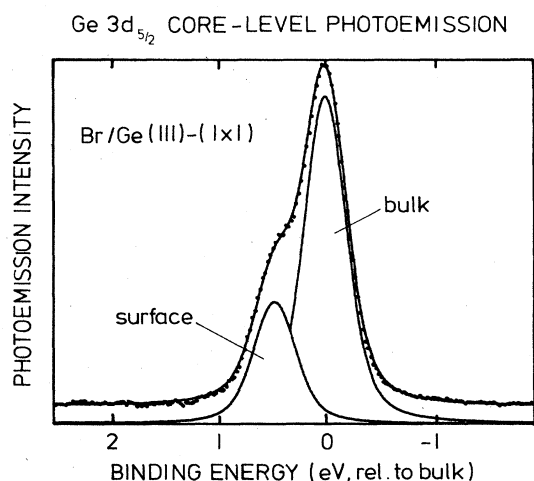


FIG. 4. Experimental and fitted Ge $3d_{5/2}$ core-level spectra for Br/Ge(111)-(1 \times 1).

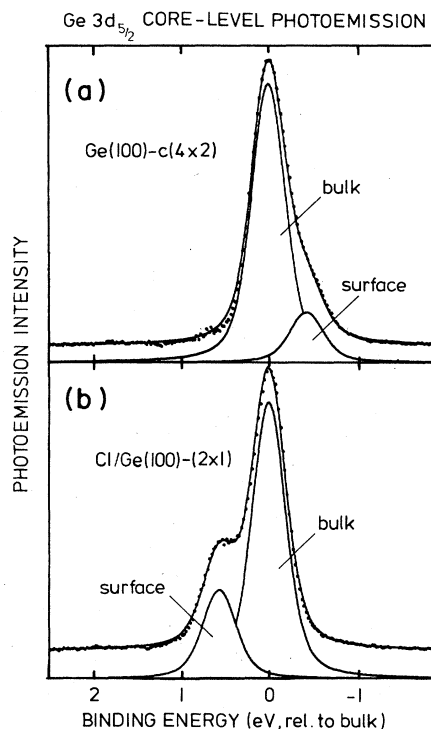


FIG. 5. Experimental and fitted core-level photoemission spectra for Ge(100)-c(4 \times 2) and Cl/Ge(100)-(2 \times 1).

two different models to obtain a relationship between the measured ratio R and the coverage Θ (in monolayers) of special surface atoms. In the continuum model⁵ R and Θ are related to each other via

$$R = 1 - \exp(-\Theta d_{\perp} / \lambda). \quad (1)$$

Here λ is the mean free path of the electrons and d_{\perp} the layer spacing in the crystal perpendicular to the surface normal. We used $d_{\perp}(100) = 1.42 \text{ \AA}$ and $d_{\perp}(111) = 1.63 \text{ \AA}$ (mean value). In the discrete-layer model⁴ one gets

$$R = \Theta [1 - \exp(-d_{\perp} / \lambda)]. \quad (2)$$

Both models give the same expression for $\Theta = 1$. Equation (2) is limited to Θ values smaller than unity. Equation (1) is valid for all Θ values.

The remaining question is to know how to fix $\Theta = 1$ ex-

TABLE I. Summary of the binding-energy shift (ΔE , relative to bulk position), the intensity ratio $R = I_S / I_{tot}$ of surface to total emission, and the coverage (Θ , in monolayers) of the Ge surface atoms on the different surfaces.

	ΔE (meV)	R	Θ
Cl/Ge(111)-(1 \times 1)	570	0.263	1
Br/Ge(111)-(1 \times 1)	470	0.272	1
Cl/Ge(100)-(2 \times 1)	570	0.244	1.03 \pm 0.06
Ge(111)-c(2 \times 8)	-260	0.248	0.93 \pm 0.08
	-760	0.069	0.25 \pm 0.03
Ge(100)-c(4 \times 2)	-430	0.152	0.62 \pm 0.05

perimentally. To do that we used the simple Cl- and Br-terminated Ge(111)-(1×1) surface.^{21,22} At this surface every dangling bond of the truncated bulk structure is saturated by a Cl or Br atom, resulting in $\Theta=1$. So we obtain the intensity of emission out of the first Ge layer in the presence of an adsorbate monolayer with the fits in Figs. 3(b) and 4. The values of R are the same within the experimental error for Cl and Br adsorption. We now assume that this intensity ratio is the same for one monolayer of Ge atoms on the clean surface. That means that we assume a uniform scattering probability by the adsorbate layer independent of the creation of a photoelectron in a bulk or surface Ge atom. This assumption seems to be justified comparing λ values obtained for GaAs(110) surfaces with this overlayer technique and other methods.²³ With our fits in Figs. 3(b) and 4 we get a mean escape depth of $\lambda=5.25\pm 0.1$ Å for a final-state energy of 25 eV. We calculated our λ value with Eqs. (1) and (2) without assuming different escape probabilities for electrons traveling in different directions to the surface.²⁴ Taking into account these corrections and an integration over the different emission directions accepted by our analyzer, the above mean-free-path value has to be increased by 3% to 5.4 Å. This value lies within the range of the result published earlier.²⁴ All Θ values obtained are summarized in Table I. The errors include uncertainties in the R factor obtained with the fits and the deviation of the λ value for the two halogen-covered (111) surfaces, as well as deviations caused by the use of the two attenuation models [Eqs. (1) and (2)].²⁵

For Cl-covered Ge(100) we get one monolayer of special surface atoms as on Cl- and Br-covered Ge(111). The energy shifts induced by Cl adsorption on Ge(100) and on Ge(111) are the same. The smaller shift after Br adsorption on Ge(111) can be explained by the smaller electronegativity of Br compared to Cl. For clean Ge(100) the value of $\Theta=0.62$ is in clear contrast to earlier measurements,⁴ where about one monolayer of special surface atoms was concluded. For clean Ge(111) two surface peaks can be distinguished: one with a smaller energy shift for about one monolayer of Ge atoms and one with a larger energy shift for one-quarter of a monolayer Ge atoms. The relative intensities I_{S1}/I_{S2} for clean Ge(111) are in agreement with earlier measurements,⁷ but the absolute coverage obtained with our analysis is significantly smaller. In the next chapter we discuss the implications of our results on surface-structure models.

IV. STRUCTURAL MODELS

Our results provide straightforward conditions for selecting structural models. For Ge(100)- $c(4\times 2)$ the coverage $\Theta=0.62\pm 0.05$ of special surface atoms is clearly closer to 0.5 than to 1.0. A natural, although perhaps oversimplified, explanation can be given by the asymmetric dimer model (see Fig. 6). This model gives half a layer of negatively charged surface atoms which correspond to the special atoms with shifted core levels. Recent scanning tunneling microscopy (STM) data²⁶ from Si(100)-(2×1) find the coexistence of symmetric and asymmetric dimers [roughly equal amounts for Si(100)].

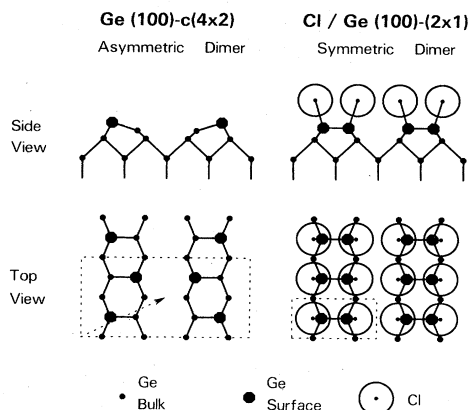


FIG. 6. Structural models for Ge(100)- $c(4\times 2)$ and Cl/Ge(100)-(2×1). The asymmetric dimer becomes symmetric upon Cl chemisorption.

Using such a model for Ge(100)- $c(4\times 2)$, we obtain 76% asymmetric and 24% symmetric dimers. The symmetric dimers might be located near domain boundaries and other defects. The Cl-covered Ge(100) surface exhibits about a full layer of surface atoms ($\Theta=1.03\pm 0.06$). The structure cannot be a terminated bulk structure as for halogens on Ge(111). We observe a clear (2×1) LEED pattern. Also, the monochloride species is seen exclusively and no dichloride as expected for the two broken bonds per surface atom of the truncated bulk structure. A natural model for the Cl/Ge(100)-(2×1) surface is the symmetric dimer model with Cl atoms saturating the remaining broken bonds (see Fig. 6). After Cl adsorption there is no reason to form asymmetric dimers because the electrons in the broken-bond orbitals can bond to Cl and have no tendency to pair up as on the clean surface.

Other structural models can be made to fit our data only by introducing defect structures. The symmetric dimer model would give a full monolayer of equivalent dimer atoms for the clean surface which is incompatible with our data. Also, the LEED pattern would be (2×1) and not $c(4\times 2)$ as observed. By removing 25% of the dimers a (2×4) structure could be built¹⁰ with symmetric dimers leading to a coverage of 0.75 of dimer atoms. After covering this structure with Cl, either 1.25 layers of surface atoms bond to Cl or 0.75 layers, depending on whether or not the Si—Si bonds at the location of the missing dimers are broken. However, the (2×4) structure should persist. The fact that we find 1.03 ± 0.06 layers of surface atoms bonding to Cl indicates only a small percentage (3±6%) of defects. A recent model¹¹ that includes chains on top of dimers is expected to give a monolayer of special chain atoms in disagreement with our data. One needs to introduce buckled chains or has to remove about 38% of the chains to make this model consistent with the data. The effect of Cl coverage is difficult to predict for such a complex structure.

For Ge(111)- $c(2\times 8)$ we propose a structural model of the type shown in Fig. 7 (see Refs. 14, 15, and 27). A quarter of a monolayer of special atoms sits above the surface (largest dots in Fig. 7) in an arrangement that repro-

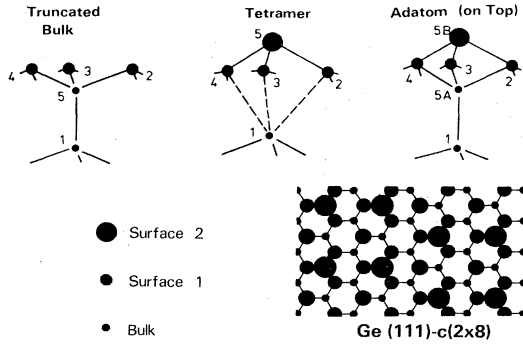


FIG. 7. Structural models for Ge(111)- $c(2 \times 8)$. Perspective views of various building blocks are shown together with a top view of two (2×8) unit cells.

duces the $c(2 \times 8)$ LEED pattern with missing quarter-order spots²⁸ and is consistent with recent STM observations.²⁹ These outermost atoms exhibit a large core-level shift. The remaining full layer of surface atoms is less exposed and accounts for the surface core level with a small

shift. Extra atoms above the surface can be produced by several ways, e.g., by putting adatoms in the hollow site,¹⁴ or in the atop site,²⁷ or by forming tetramers via a bond flip.^{15,27} The chemisorption behavior of Ge(111)- $c(2 \times 8)$ is easy to understand in the tetramer model. Upon chemisorption of Cl or Br, the bond flip is reversed and a simple (1×1) terminated bulk structure results. With adatoms it is difficult to explain the observed transition to (1×1) unless the adatoms are completely etched away by the halogen at room temperature. We have found no evidence for intermediate etching products such as GeCl_2 or GeCl_3 species at saturation coverage.

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