

## Photoemission surface core-level study of sulfur adsorption on Ge(100)

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(Received 7 November 1986)

The interaction of elementary sulfur with Ge(100)(2×1) surfaces was investigated using low-energy electron diffraction, Auger-electron spectroscopy, and photoemission core-level spectroscopy. Chemisorption of sulfur results in a binding-energy shift of the Ge 3*d* core-level electrons of  $\Delta E = 0.33 \pm 0.01$  eV per S—Ge bond. The adsorbed sulfur dissociates and leads to an ordered (1×1) reconstruction with one S atom per surface unit cell. The adsorbed sulfur atoms are bonded on bridge sites. Sulfur deposition exceeding one monolayer is possible, probably due to defects; the excess can be selectively thermodesorbed. During room-temperature adsorption, no S islands are formed. Thermodesorption is destructive, possibly etching.

### I. INTRODUCTION

Stoichiometric saturation of all surface valences of a semiconductor surface may result in a (1×1) reconstruction of high order and stability. Such ideally terminated surfaces as As/Si(111)(1×1), As/Ge(111)(1×1), and Cl/Ge(111)(1×1) attract current interest.<sup>1–3</sup> On the one hand these surfaces are simple model systems for the investigation of the bonding mechanisms which determine the reconstruction of semiconductor surfaces; on the other hand these ideally (1×1) reconstructed surfaces might have applications in future molecular-beam epitaxy (MBE) layer-growing techniques.

Sulfur and higher chalcogens are prospective candidates as adsorbates to obtain an ideal (1×1) termination of the bivalent (100) surfaces of Si and Ge (oxygen is known to penetrate and form SiO<sub>2</sub> and GeO<sub>2</sub> instead<sup>4,5</sup>). Recently, we investigated the interaction of sulfur with these two surfaces. In this paper we show that sulfur adsorption on Ge(100) can indeed yield an ideally terminated surface; an analogous result for the Si(100) surface was not achieved.<sup>6</sup>

A lot of work has been done on sulfur adsorption on metal surfaces where the standard preparation method uses H<sub>2</sub>S. Applying this technique to semiconductor surfaces leads to coadsorption of H, HS, and S. The hydrogen cannot be removed selectively. Some investigations have been performed on such mixed systems.<sup>7,8</sup> In order to obtain pure sulfur adsorption we prepared our surfaces by exposure to a molecular beam of elementary sulfur.

In this paper we show that it is possible to establish a structural model for S/Ge(100)(1×1) by monitoring the Ge 3*d* surface core-level photoemission during adsorption and desorption of sulfur. The conclusions are drawn from the shifted surface contributions according to different oxidation states of the first layer of Ge atoms. The major results are as follows. S/Ge(100)(1×1) is an ideally terminated surface, the sulfur coverage being one atom per Ge surface atom. The adsorbed sulfur is bonded on bridge sites. No large sulfur islands are formed during room-temperature adsorption. The thermodesorption process is destructive, possibly etching (desorption of GeS).

### II. EXPERIMENTAL

We used Ge samples of low *n*-type doping concentrations in order not to affect the measured photoelectron spectra by changes of the band bending within the escape depth of the photoelectrons.<sup>9</sup> The surfaces were prepared with repeated cycles of mild sputtering (600–800-eV Ar<sup>+</sup>) and heating to about 600°C. This resulted in a (2×1) low-energy electron diffraction (LEED) pattern. The sulfur was produced *in situ* under UHV conditions by dissociation of Ag<sub>2</sub>S in a solid-state electrochemical cell<sup>10</sup> in a separate chamber connected to the vacuum system. All surfaces were checked before and after sulfur adsorption by LEED and Auger-electron spectroscopy (AES) analysis.

The AES intensity of sulfur *LMM* emission reaches saturation for room-temperature adsorption on Ge(100), the covered surface shows a (1×1) LEED pattern. The quality of the LEED pattern can be improved by carefully annealing the sample. The sulfur covered surface is inert with respect to residual gas contamination and does not show any detectable changes after ~48 hours in UHV.

The photoemission 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.<sup>11</sup> The photoelectrons were analyzed with an ellipsoidal mirror display spectrometer<sup>12,13</sup> operated in the angle-integrating mode with an acceptance cone of about 90°. The Ge 3*d* electrons were excited in the photon energy range  $h\nu = 40\text{--}60$  eV with  $h\nu = 60$  eV giving the best surface sensitivity.

### III. PHOTOEMISSION RESULTS

#### A. Evaluation procedure

Figure 1 shows the spin-orbit splitting and the determination of the bulk emission line shape. Figure 1(a) demonstrates the decomposition of an experimental Ge 3*d* core-level spectrum into two equally shaped contributions

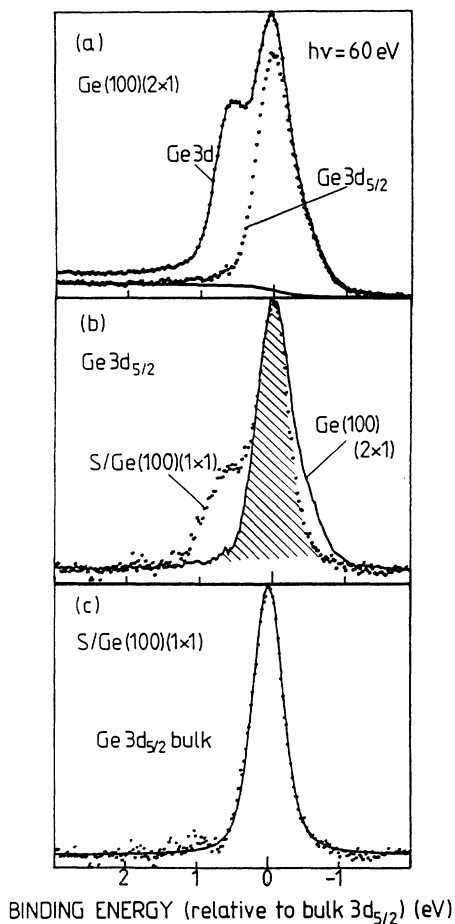


FIG. 1. Ge  $3d$  core-level photoemission spectra for clean and sulfur-covered Ge(100) surfaces. (a) Spin-orbit splitting and secondary electron background. (b) Determination of bulk emission. (c) Surface-bulk deconvolution for S/Ge(100)( $1\times 1$ ).

( $3d_{3/2}$  and  $3d_{5/2}$ ; spin-orbit splitting  $\Delta^{LS}=0.585\pm 0.01$  eV,  $3d_{3/2}$  to  $3d_{5/2}$  branching ratio  $B=0.68\pm 0.02$ ) and the secondary electron background. After subtraction of the  $3d_{3/2}$  contribution and the background we fit the Ge  $3d_{5/2}$  spectra using a Voigt line shape (convolution of a Gaussian and a Lorentzian). In order to keep the number of fit parameters small the line shape (Lorentzian and Gaussian linewidth) is determined independently by the following procedure and kept constant for all fits. Figure 1(b) shows Ge  $3d_{5/2}$  spectra of a clean and a sulfur terminated sample. The surface contribution of the clean (sulfur covered) surface is shifted to lower (higher) binding energy relative to the bulk line; therefore the hatched area can directly be regarded as the bulk contribution and is used to determine the line shape [Lorentzian linewidth: 190 meV full width at half maximum (FWHM); Gaussian broadening: 390 meV FWHM]. The Ge  $3d_{5/2}$  spectrum of S/Ge(100)( $1\times 1$ ) was decomposed into two equally shaped contributions according to bulk and surface emission (energy splitting:  $\Delta E=0.665$  eV; surface to bulk in-

tensity ratio  $r=0.33$ ). In Fig. 1(c) the hence obtained bulk contribution is compared with the line shape determined above [compare Fig. 1(b)]. The identity of the two curves confirms the determination of the bulk line parameters and shows that the surface and the bulk contribution of S/Ge(100)( $1\times 1$ ) are equally shaped. This line shape is used for evaluation of all Ge  $3d_{5/2}$  spectra.

### B. Determination of coverage

Figure 2 shows experimental and fitted Ge  $3d_{5/2}$  core-level spectra of the clean [Fig. 2(a)] and sulfur-terminated [Fig. 2(b)] surface. The surface binding-energy shift  $\Delta E$  and the intensity ratio  $R=I_s/I_{tot}=r/(1+r)$  of the surface emission ( $I_s$ ) relative to the total  $3d_{5/2}$  emission ( $I_{tot}$ ) is determined from these spectra. We find for (a) Ge(100)( $2\times 1$ ):  $\Delta E=-0.44\pm 0.01$  eV,  $R=0.16\pm 0.015$ ; and for (b) S/Ge(100)( $1\times 1$ ):  $\Delta E=0.665\pm 0.01$  eV,  $R=0.25\pm 0.015$ .

Now we determine the quantity of surface atoms (measured in monolayers) which contribute to the shifted core-level peak of S/Ge(100)( $1\times 1$ ). In the discrete layer model<sup>3,14</sup> the intensity ratio  $R$  and the coverage  $\Theta$  (in monolayers) of the Ge surface atoms contributing to the shifted peak are related to each other via

$$R=[1-\exp(-d/\lambda)]\Theta, \quad (1)$$

where  $\lambda$  is the mean free path of the electrons and  $d$  the layer spacing (1.42 Å) perpendicular to the surface. For Ge(100)( $2\times 1$ ) the coverage  $\Theta$  corresponding to the shifted surface peak was determined as being  $\Theta=0.62\pm 0.05$ ;<sup>3</sup> there the calibration of  $\Theta=1$  was achieved by chlorine saturation adsorption. Using this value of  $\Theta$  for the clean

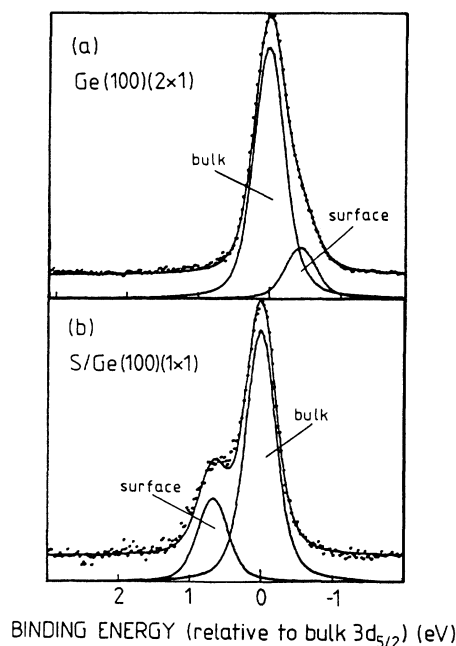


FIG. 2. Experimental and fitted Ge  $3d_{5/2}$  core-level spectra for Ge(100)( $2\times 1$ ) and S/Ge(100)( $1\times 1$ ).

surface and  $R = 0.16$ , we obtain  $R/\Theta = [1 - \exp(-d/\lambda)] = 0.26 \pm 0.03$  and hence  $\lambda = 4.7 \pm 0.7$  Å and  $\Theta = 0.96 \pm 0.13$  for S/Ge(100)(1×1). From this we conclude that the complete first layer of Ge atoms ( $\Theta = 1$ ) contributes to the shifted peak for S/Ge(100)(1×1). With this conclusion the determination of the escape depth can be improved; we obtain  $\lambda = 4.95 \pm 0.35$  Å for the final-state energy of 30 eV. This value was calculated without assuming different escape probabilities for electrons traveling in different directions to the surface.<sup>15</sup> Taking into account these corrections and integrating over the acceptance cone of our analyzer the above mean free path has to be increased by 3% to 5.1 Å. This value lies within the range of the result published earlier.<sup>15</sup>

As we have shown the complete first Ge layer contributes to one shifted peak and is therefore in the same oxidation state. In other words, all Ge surface atoms are bonded to the same number of sulfur atoms. As sulfur is bivalent and each Ge atom of the unreconstructed surface has two dangling bonds, one might expect a coverage of

one sulfur atom per Ge surface atom, which is therefore in the oxidation state 2+. This can be proved by detection of the other oxidation states. Their appearance can be expected at defects, and therefore we investigated a stepped surface. Figure 3 shows Ge 3*d* core-level spectra taken from a sulfur-covered 6° vicinal surface. In Fig. 3(a) the original spectra of this surface and of a S/Ge(100)(1×1) surface are compared. From the additional emission of states with higher binding energy we see directly that the first Ge layer of the smooth S/Ge(100)(1×1) surface cannot be in the highest possible oxidation state which is 4+ as in GeS<sub>2</sub>. It is known<sup>4,5,16,17</sup> that different oxidation states result in approximately equidistant binding-energy shifts. Figure 3(b) illustrates that the spectrum of the vicinal surface cannot be fitted under the assumption that the binding-energy shift of  $\Delta E = 0.665$  eV [of S/Ge(100)(1×1)] corresponds to the oxidation state 1+, because this assumption allows only additional states of too high binding energy. As shown in Fig. 3(c) four oxidation states are necessary to explain the data; the binding energy of the Ge 3*d* electrons is shifted by  $0.33 \pm 0.01$  eV per S—Ge bond. Regarding the S/Ge(100)(1×1) surface, we hence have identified the oxidation state of the first Ge layer as the 2+ state which corresponds to a coverage of one sulfur atom per Ge surface atom.

### C. Adsorption geometry

As shown above the S/Ge(100)(1×1) surface has a coverage of one sulfur atom per (1×1) surface unit cell. As it is well known that S-Ge compounds have covalent bonding character, we exclude any other adsorption geometry than those shown in Fig. 4 (especially the hollow site position—typical only for ionic and metallic bonding—can be ruled out). The two different models of Fig. 4 can be distinguished by investigation of low-coverage (submonolayer) adsorption. Assuming that the adsorbed sulfur atoms do not form large islands (this will be shown below), one expects two oxidation states (1+, 2+) in the case of bridge-site adsorption, but only one (2+) in the case of top-site adsorption. This idea is illustrated in Fig. 5. For this conclusion it is necessary that

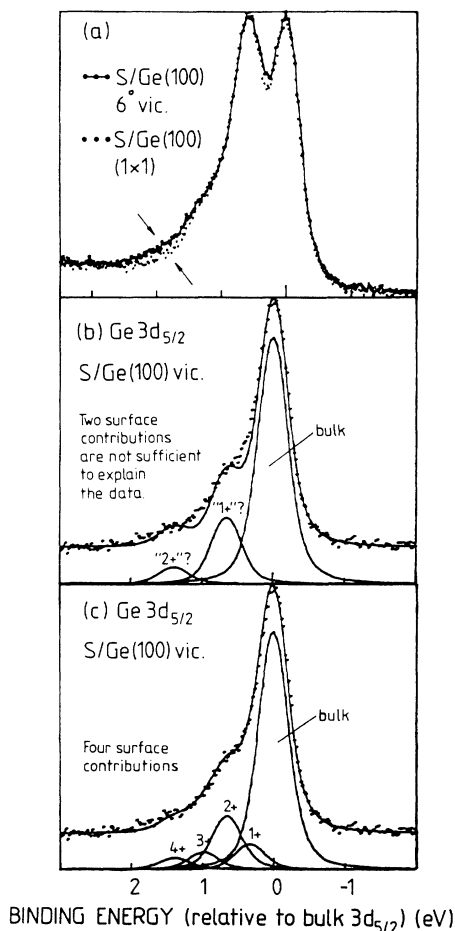


FIG. 3. Ge 3*d* core-level photoemission spectra of a 6° vicinal Ge(100) surface. (a) Comparison with the spectrum for the S/Ge(100)(1×1) surface. (b) The vicinal surface shows more than two oxidation states. (c) Four oxidation states are necessary to explain the data.

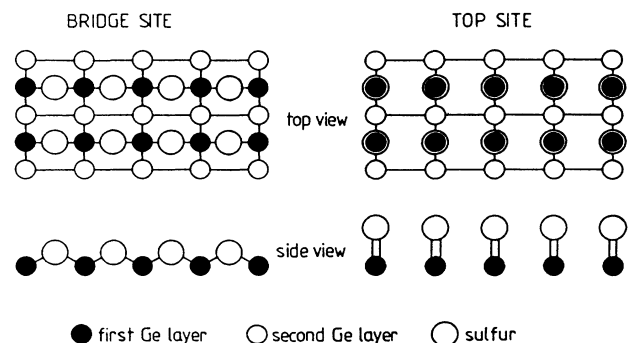


FIG. 4. Possible adsorption geometries for S/Ge(100)(1×1). As shown below, the bridge-site model is the correct one.

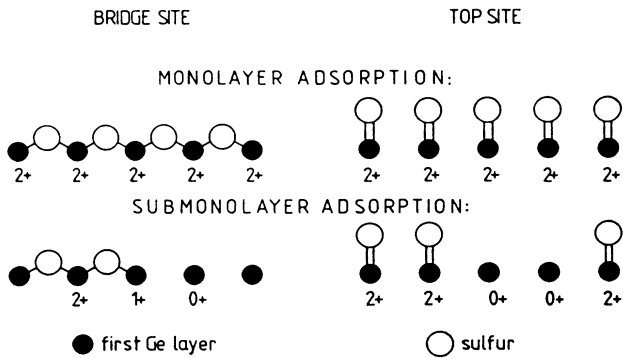


FIG. 5. Bridge-site and top-site bonding can be distinguished by the appearance of the oxidation state 1+ in the case of low-coverage adsorption.

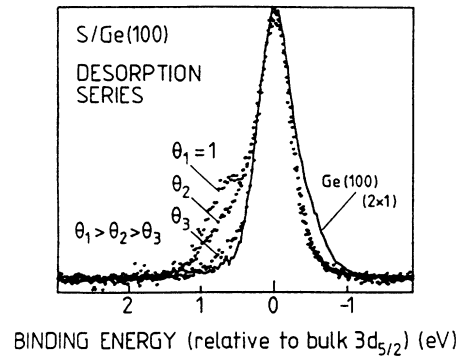


FIG. 7. Ge  $3d_{5/2}$  core-level spectra of a thermodesorption series of S/Ge(100) and of Ge(100)( $2\times 1$ ).

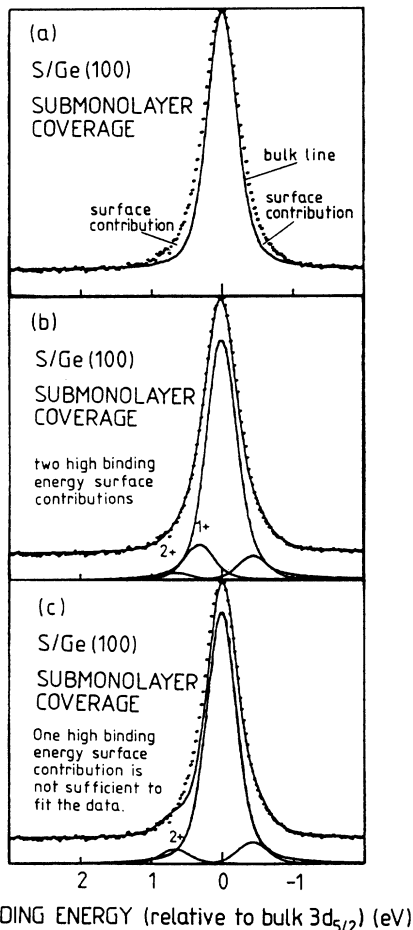


FIG. 6. Ge  $3d_{5/2}$  core-level spectra of a submonolayer covered Ge(100) surface which was prepared by low exposure. (a) A low-binding-energy surface contribution [clean Ge(100)( $2\times 1$ ):  $\Delta E = -0.44$  eV] is preserved (in opposite to low-coverage preparation by thermodesorption, see Fig. 7). (b) and (c) The fit of the experimental spectrum requires a strong 1+ contribution as expected for bridge-site adsorption geometry. (c) shows that it is impossible to fit the data without it.

the adsorption process does not result in large sulfur islands. Otherwise, the spectra would be dominated by the 2+ oxidation state anyway; in the case of bridge-site adsorption only a weak 1+ contribution due to the borders of the islands might appear.

We prepared submonolayer sulfur coverages by low exposure at room temperature. Figure 6 shows a corresponding spectrum. As can be seen in Fig. 6(a) surface contributions appear on both sides of the bulk line. The fit of Fig. 6(b) is characterized by a strong contribution of the oxidation state 1+. Hence we draw two conclusions: (i) The sulfur is bridge bonded and (ii) does not form large islands during room-temperature adsorption. To show clearly that the fit of the experimental spectrum requires a 1+ contribution we demonstrate in Fig. 6(c) that it is impossible to fit the data without it.

In addition to the experiment shown above we prepared submonolayer sulfur coverages by partial thermodesorption after saturation adsorption. This preparation technique yields different results and discloses another interesting effect. In Fig. 7 core-level spectra of a desorption series together with a spectrum of the clean Ge(100)( $2\times 1$ ) surface are shown. The reappearance of the surface contribution at the low-binding-energy side [Ge(100)( $2\times 1$ ):  $\Delta E = -0.44$  eV] after desorption is inhibited [compare Fig. 7 with Fig. 6(a)]. The thermodesorption process does not recreate an atomically well-defined surface. Possibly this can be explained by an etching process (desorption of GeS).

#### ACKNOWLEDGMENTS

We would like to thank the staff of BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung, Berlin, Germany) for support. We thank D. Rieger, F. J. Himpsel, K. Wandelt, and W. Moritz for valuable discussions. This work has been supported by the Bundesministerium für Forschung und Technologie (Bonn, Germany) from funds for synchrotron radiation; one of us (T.W.) has received support from the Studienstiftung des Deutschen Volkes (Bonn, Germany).

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