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Final-state pseudopotential theory for the Ge 3*d* core-level shifts on the Ge/Si(100)-(2×1) surface

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We have calculated the Ge 3*d* core-level shifts on the Ge/Si(100)-(2×1) surface using the final-state pseudopotential theory. We find that the core levels of the up and down atoms within the asymmetric Ge dimer are separated by 0.54 eV at 1-ML Ge coverage, 0.43 eV at 2-ML Ge coverage, and 0.40 eV at the clean Ge(100) surface. Such a large core-level shift represents a substantial charge asymmetry within the Ge dimer. The present results agree well with recent x-ray photoemission spectroscopy (XPS) data on the Ge(100) surface, but disagree with XPS data on the adsorbed Ge/Si(100) surface.

I. INTRODUCTION

As a prototype of lattice-mismatched semiconductor heterojunctions, the mode of Ge growth on Si(100) has been a subject of many studies for several years. The initial growth of Ge on Si(100) is known to follow a layer-by-layer pattern up to a thickness of several atomic layers, where the Ge layers maintain the (2×1) dimer structure.[1,2] Especially for the 1-ML Ge coverage, recent experimental[3,4] and theoretical[5–7] studies are in good agreement that the structure of the top-layer Ge dimers on Si(100) is asymmetric.

Despite the evidence of the asymmetric dimer structure in Ge/Si(100), however, there remains a controversy regarding the extent of charge asymmetry between the two Ge dimer atoms. Recently, Lin, Miller, and Chiang[8] studied the Ge 3*d* core levels in Ge/Si(100) for several different Ge coverages using the x-ray photoemission spectroscopy (XPS). They observed only a single component (S) at submonolayer Ge coverages, and two surface components (S and S') at about 2-ML Ge coverage. In their analysis based on the layer-by-layer Ge growth model, the S component was associated with the top-layer Ge dimer atoms and the S' component, with the second-layer Ge atoms. That is, they concluded that the core-level separation (and the underlying charge asymmetry) between the two Ge dimer atoms in Ge/Si(100) is negligible. As mentioned before, however, the top-layer Ge dimers at 1-ML coverage are known to be strongly asymmetric in geometry:[4–7] the dimer tilt angle amounts to 12°–17° and the calculated energy gain involved in the dimer tilt is as large as about 0.35 eV. A large charge asymmetry and the corresponding core-level separation between the two Ge dimer atoms on Si(100) is expected. As a matter of fact, this is what we have found in the case of the clean Ge(100) surface. The structure of dimers on Ge(100) is also asymmetric[9,10] and, for this surface, a substantial separation (about 0.5 eV) of Ge 3*d* core levels between the up and down dimer atoms has been reported in very recent XPS studies.[11,12]

In the present work, we investigate the Ge 3*d* core-level shifts in the Ge/Si(100)-(2×1) surface for several Ge coverages using the final-state pseudopotential theory of Pehlke and Scheffler,[13] which has been successfully applied for the Si(100) and Ge(100) surfaces. The key result is that the core-level separation between the up and down dimer atoms is 0.54 and 0.43 eV at 1-ML and 2-ML Ge coverages, respectively, and this value is saturated to 0.40 eV in Ge(100). That is, the asymmetric dimer structure results in a substantial charge transfer and the corresponding large core-level shift between the up and down atoms in a dimer. Such a large core-level splitting between the up and down atoms, which is consistent with the results of recent XPS studies on Ge(100),[11,12] does not support the conclusion of the XPS study of Lin, Miller, and Chiang on Ge/Si(100).[8]

The rest of the text is organized as follows. In Sec. II, the calculational scheme is described. In Sec. III, we present the results for Ge 3*d* core-level shifts on the Ge/Si(100)-(2×1) surface and compare with experimental ones. Finally, a summary is given in Sec. IV.

II. FINAL-STATE PSEUDOPOTENTIAL THEORY

The binding energy (ξ) of a core electron in a solid is defined as a difference in the total energy of the system between the corresponding core-hole ionized state and the initial ground state,

$$\xi = E(N-1;\ \text{core hole}) - E(N)\ , \tag{1}$$

where N is the number of electrons in the ground state. The core-level binding energies are sensitive to the surrounding electronic configuration, and, therefore, surface core-level shifts measured by x-ray photoelectron spectroscopy can provide useful information on the atomic and electronic structures at surfaces. For a surface system the core-level binding energies are given by

$$\xi_S = E_S(N-1) - E(N)\ , \tag{2}$$

$$\xi_B = E_B(N-1) - E(N)\ , \tag{3}$$

where E_S and E_B are the total energies of the system containing a core hole in a surface atom and in a bulk atom, respectively. Hence, the surface core-level shift relative to the bulk one can be evaluated by

$$\Delta\xi=\xi_S-\xi_B=E_S(N-1)-E_B(N-1)\ . \tag{4}$$

We calculate the surface core-level shift employing the final-state pseudopotential theory introduced by Pehlke and Scheffler[13] where the effect of a photon-induced core hole in solids is represented by the atomic pseudopotentials generated from an excited atom with the corresponding screened core hole.

The total energies of the system are calculated using a momentum-space formalism[14] within the local-density approximation[15] (LDA) and norm-conserving pseudopotential scheme.[16] We treat the many-electron interactions using the Ceperley-Alder LDA exchange-correlation functional parametrized by Perdew and Zunger.[17] The atomic pseudopotentials of Si and Ge are generated in a separable form of Kleinman and Bylander[18] from the ground-state atomic configurations using the generalized norm-conserving pseudopotential scheme.[16] We generate the atomic pseudopotentials for the Ge atom with a screened $3d$ core hole from the excited atomic configuration of $3d^94s^24p^3$.

We simulate the Ge/Si(100) surface by a periodic slab geometry: the unit supercell consists of 12 atomic and 4 vacuum layers. In order to make the interactions of nearby core holes in the supercell negligible, we treat the (2×1) structure in an expanded (2×2) supercell. We employ a plane-wave basis with the kinetic energy up to 10 Ry and use a uniform grid of 16 k points for the (2×2) surface Brillouin-zone integration.

III. RESULTS

In the present work, we calculate the surface shifts of the Ge $3d$ core level for three different Ge structures: the Ge/Si(100)-(2×1) surface with 1-ML Ge coverage, the same one with 2-ML Ge coverage, and the clean Ge(100)-(2×1) surface (see Fig. 1). In the following these systems will be denoted for convenience by Ge–1 ML, Ge–2 ML, and Ge(100), respectively.

First, we determine the equilibrium atomic structure for each system by relaxing the Ge and Si atoms in the top-five surface layers along the calculated Hellmann-Feynman forces. An abrupt Ge/Si interface without intermixing is assumed for Ge–1 ML and Ge–2 ML, based on experimental evidences.[4,19,20] The atomic relaxation continues until the remaining forces on surface atoms are all within 0.1 eV/Å. We find in all systems that the top-layer Ge dimers are strongly asymmetric: the asymmetric structure is energetically favored over the symmetric one by 0.35 eV/dimer at Ge–1 ML and by 0.28 eV/dimer at Ge(100). The calculated Ge-dimer geometry (bond length and tilt angle) for each system is shown in Table I. It is noticeable that the dimer bond length is converged to that of Ge(100) even at 2-ML coverage. The present results agree well with those of the previous calculations on Ge–1 ML and Ge(100).[5,9]

TABLE I. Calculated Ge dimer bond length (d_D) and tilt angle (θ) for the Ge/Si(100)-(2×1) and Ge(100)-(2×1) surfaces.

		d_D (Å)	θ (degree)
Present	1 ML Ge/Si(100)	2.39	16
	2 ML Ge/Si(100)	2.45	18
	Ge(100)	2.46	19
Krüger and Pollmann[a]	1 ML Ge/Si(100)	2.39	17
	Ge(100)	2.41	19
Needels *et al.*[b]	Ge(100)	2.46	13

[a] Reference 5.

[b] Reference 9.

The calculated surface shifts of the Ge $3d$ core level in Ge–1 ML, Ge–2 ML, and Ge(100) are summarized in Fig. 2 in comparison with the experimental results.[8,11] In Ge–1 ML, where the Ge atoms form the top-layer asymmetric dimers, the core levels S_1 (for the up atom) and $S_{1'}$ (for the down atom) are well separated by 0.54 eV, which is a strong indication of a large charge asymmetry within the dimer atoms. This separation of S_1 and $S_{1'}$ remains as large as 0.43 eV at 2-ML Ge coverage. In addition, Ge–2 ML shows two more core levels (S_2 and $S_{2'}$) coming from the second-layer Ge atoms. The core-level shifts of S_2 and $S_{2'}$ relative to S_1 are 0.21 and 0.53 eV, respectively. This separation of S_2 and $S_{2'}$ ($=0.32$ eV) is due to the inequivalence of the positions of the two second-layer Ge atoms in the present (2×1) asymmetric dimer geometry.

In Ge(100), the core-level separation of S_1 and $S_{1'}$ is saturated to 0.40 eV and that of S_2 and $S_{2'}$ is 0.28 eV. In fact, these values are comparable to the results of Ge–2 ML. This rapid convergence of the surface core levels with respect to the Ge coverage is a result of the similar convergence of the Ge dimer structure as mentioned in Table I. The shift of the surface core level (S_1) relative to the bulk one (B) is calculated by -0.73 eV (i.e., lower binding-energy shift of S_1).[21]

The present result on Ge(100) compares well with the previous calculations of Pehlke and Scheffler,[13] where the surface core-level shifts were found to be -0.67 eV for the up atom, -0.39 eV for the down atom, and -0.16 eV for the second-layer atoms. A few differences can be attributed to the fact that Pehlke and Scheffler studied

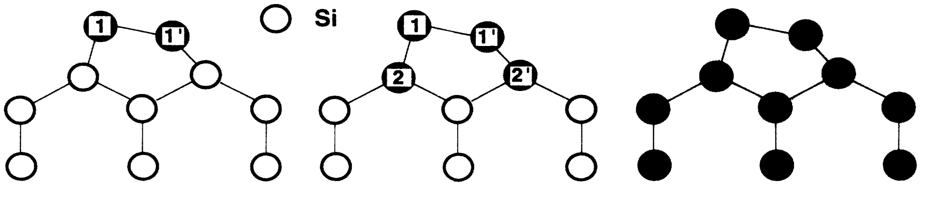

FIG. 1. Schematic diagram of the Ge/Si(100)-(2×1) and Ge(100)-(2×1) surfaces: (a) 1-ML Ge coverage, (b) 2-ML Ge coverage, and (c) clean Ge(100)-(2×1). All figures are given in side view from [011] direction. Ge atoms 1 and 1′ (2 and 2′) are in the top (second) layer.

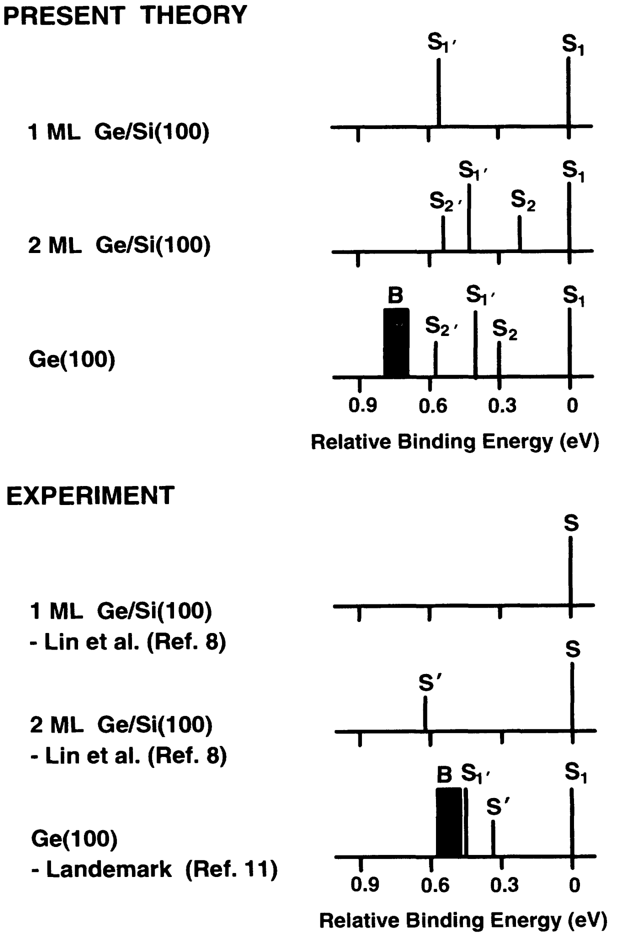

FIG. 2. Calculated Ge 3*d* core-level shifts on the Ge/Si(100)-(2×1) and Ge(100)-(2×1) surfaces in comparison with the experimental ones. The binding energies are given relative to the core level of the up atom of the asymmetric dimer.

the $p(2\times2)$ Ge(100) geometry where the buckled Ge dimers are alternating along the dimer row, while the present one is the $p(2\times1)$ surface. For example, Pehlke and Scheffler obtained just a single component for the second-layer atoms, since those atoms are equivalent in the $p(2\times2)$ geometry.

The present calculations on Ge(100) support recent XPS results[11,12] in which the surface component from the down atoms (i.e., $S_{1'}$) was resolved near the bulk peak. The two surface components (S_1 and $S_{1'}$) originating from the up and down atoms are separated by about 0.5 eV. In fact, we find in Fig. 2 that the arrangements of the surface-related core levels for Ge(100) are very similar between the present results and the experiment of Landemark.[11] We also find that the calculated surface core levels tend to be overshifted to the lower binding side compared to the experimental values. As pointed out by Pehlke and Scheffler,[13] this discrepancy can be attributed to the possible overestimation of the screening of the surface core holes.

In their recent XPS study of the Ge/Si(100)-(2×1) surface, Lin, Miller, and Chiang[8] obtained from the observed Ge 3*d* core-level spectra only a single dominant component (S) at Ge coverages below 1 ML, and decomposed two surface components (S and S') at about 2 ML (see Fig. 2). They concluded that the S component is associated with the top-layer Ge atoms (i.e., both of dimer atoms) and the S' component, with the second-layer atoms. Accordingly, a large core-level splitting between the up and down atoms of the Ge dimers was ruled out. This result is in conflict with the present results on Ge–1 ML and Ge–2 ML, and also with the experimental and theoretical fact that the surface components originating from the up and down atoms of a dimer in Ge(100) are well resolved in energy by about 0.4–0.5 eV.

Moreover, the separation of S and S' (0.63 eV) at 2-ML Ge coverage in the experiment of Lin *et al.* is too large compared with that of S_1 and S' (0.33 eV) reported by Landemark on Ge(100) (see Fig. 2).[22] This large discrepancy is not acceptable from the point of view that the surface-related core levels change little from Ge–2 ML to Ge(100) in our calculations. Rather, it is notable that the S and S' of Lin *et al.* are similar in position to the calculated S_1 and $S_{1'}$ at Ge–1 ML.

In conclusion, a close examination of the surface core-level shifts shown in Fig. 2 leads us to interpret that the S (S') component of Lin *et al.* comes from the up (down) atom in the top-layer Ge dimer. Then, for a consistency, the actual coverage of Ge in the experiment of Lin, Miller, and Chiang[8] should be scaled to one half of the cited values; i.e., their 2-ML coverage is in fact 1-ML coverage and their 1-ML coverage corresponds to $\frac{1}{2}$ ML. In that case, the single component S observed at about $\frac{1}{2}$-ML coverage (cited as 1 ML in the paper of Lin *et al.*) could be associated with the Ge atoms deposited on the up-atom dimer sites. This interpretation is based on the assumption that the up-atom dimer site in Si(100) is preferred for the Ge adsorption at low coverage. We have found in our total-energy calculations for the $\frac{1}{2}$-ML Ge coverage that the up-atom dimer site is more stable than the down-atom site by about 0.13 eV/atom in adsorption energy. However, this assumption is subject to experimental investigation since detailed structural information

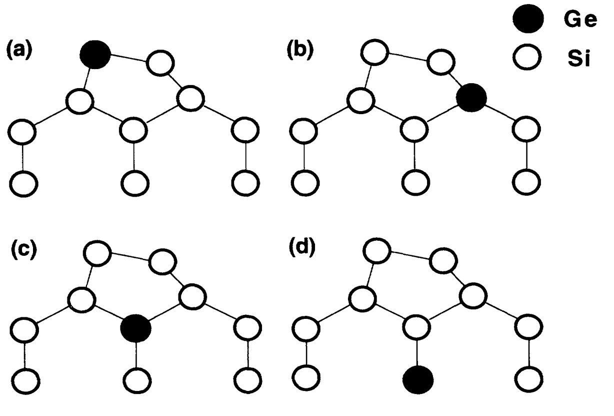

FIG. 3. Several model structures with $\frac{1}{2}$-ML deposition of Ge: Ge is located in (a) the top layer, (b) the second layer, (c) the third layer, and (d) the fourth layer.

on the Ge/Si(100) interface at the initial stage (i.e, at submonolayer Ge coverages) of Ge deposition is not available.

Rowe and Wertheim[23] have already pointed out, based on the Ge interdiffusion model, the possibility of wrong calibration of Ge coverage in the experiment of Lin *et al.*, too. The surface Ge coverage can differ significantly according to the initial growth mode of Ge on Si(100). In order to investigate the possibility of Ge interdiffusion to Si(100), we consider the energetics for several interdiffusion structures with a $\frac{1}{2}$-ML deposition of Ge (see Fig. 3). We find that the adsorbed Ge atoms is the most stable at the up-atom dimer sites: the adsorption energy decreases in deeper layers by 0.23 eV/atom at the second layer, 0.34 eV at the third layer, and 0.35 eV at the fourth layer. The present result shows that the mixing of Ge into the Si layers is energetically unfavorable, in good agreement with existing experimental evidences.[4,19,20] Hence, it is not likely that the interdiffusion model is the very origin of the coverage problem questioned to the experiment of Lin *et al.*

IV. SUMMARY

We have used the final-state pseudopotential theory to calculate the surface shifts of the Ge 3*d* core level on the Ge/Si(100) and clean Ge(100) surfaces. For both systems the structure of the top-layer Ge dimers are asymmetric and the calculated core-level shifts between the up and down atoms in the dimer amount to 0.40–0.54 eV, indicating an apparent charge asymmetry within the dimer. From the comparison of the present theory and recent XPS data[11,12] on the Ge(100) surface, we concluded that the Ge coverages in the previous XPS study[8] of the Ge/Si(100) surface are likely to have been overestimated by a factor of 2.

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[1] H.-J. Gossmann, L. C. Feldman, and W. M. Gibson, Surf. Sci. **155**, 413 (1985).

[2] Y.-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. **65**, 1020 (1990).

[3] F. Iwawaki, H. Kato, M. Tomitori, and O. Nishikawa, Ultramicroscopy **42 – 44**, 895 (1992).

[4] E. Fontes, J. R. Patel, and F. Comin, Phys. Rev. Lett. **70**, 2790 (1993).

[5] P. Krüger and J. Pollmann, Phys. Rev. Lett. **72**, 1130 (1994).

[6] J. M. Jin and L. J. Lewis, Phys. Rev. B **49**, 2201 (1994).

[7] J. H. Cho and M. H. Kang, Phys. Rev. B **49**, 13 670 (1994).

[8] D.-S. Lin, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **67**, 2187 (1991).

[9] M. Needels, M. C. Payne, and J. D. Joannopoulos, Phys. Rev. Lett. **58**, 1765 (1987).

[10] J. A. Kubby, J. E. Griffith, R. S. Becker, and J. S. Vickers, Phys. Rev. B **36**, 6079 (1987).

[11] E. Landemark (unpublished), taken from citation 16 of Ref. 13.

[12] W. Ranke and J. Wasserfall, Surf. Sci. **292**, 10 (1993).

[13] E. Pehlke and M. Scheffler, Phys. Rev. Lett. **71**, 2338 (1993).

[14] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4401 (1979).

[15] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[16] D. R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979); D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).

[17] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[19] M. Diani, D. Aubel, J. L. Bischoff, L. Kubler, and D. Bolmont, Surf. Sci. **291**, 110 (1993).

[20] N. Ikarashi, K. Akimoto, T. Tatsumi, and K. Ishida, Phys. Rev. Lett. **72**, 3198 (1994).

[21] The bulk value was determined by averaging the core levels in the innermost layers of the 16-layer Ge slab.

[22] In their XPS study of the Ge(100)-(2×1) surface, Yang *et al.* [see J. Vac. Sci. Technol. B **20**, 2013 (1992)] resolved only two surface components S and S', similar to the results of Lin *et al.* However, the separation of their S and S' (0.36 eV) is also much smaller than that of Lin *et al.* From the comparison of energy levels, we can identify the S and S' of Yang *et al.* with the S_1 and S' of Landemark. Thus, it would be reasonable to assign the S and S' of Yang *et al.* to the up atoms of the dimer and the second-layer atoms, respectively. It is likely that the surface component corresponding to the S' of Lin *et al.* was not resolved from the bulk peak in the work of Yang *et al.*

[23] J. E. Rowe and G. K. Wertheim, Phys. Rev. Lett. **69**, 550 (1992).