Dimer-T₃ reconstruction of the Sm/Si(100)(2×3) surface studied by high-resolution photoelectron spectroscopy and density functional theory calculations

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Silicon dimer–containing reconstructions on Si(100) can be induced by submonolayer amounts of rare earth (RE) metals. The tilt of dimer bonds in such reconstructions can be controlled by the coverage and electronic properties of RE adsorbates. In this study, we have utilized improved high-resolution photoelectron spectroscopy with the synchrotron radiation and density functional theory (DFT) calculations to exploit the structural and electronic properties of the Sm/Si(100)(2 × 3) system. A careful analysis of photoelectron spectra, in combination with DFT calculations of surface core-level shifts for silicon atoms in energetically plausible structural models, has allowed us to establish the favorable atomic configuration of Sm/Si(100)(2 × 3) with a buckled Si dimer and to explain characteristic features of Si 2p line shape in detail. It is shown that the dimer buckling leads to a significant core-level binding-energy splitting of the first-layer Si atoms, affecting the lower-binding-energy region of Si 2p spectra drastically. An interpretation of the Si 2p line shape for RE/Si(100)(2 × 3) that is based on combined initial state and complete screening data is suggested. The mechanism underlying the buckling and symmetrization of silicon dimers in RE/Si(100) reconstructions is discussed.

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I. INTRODUCTION

A dimer formed by pairing of uppermost layer atoms is known to be a basic structural element (building block) on the (100) surfaces of semiconductor materials. On clean silicon and germanium (100), the dimerization in the topmost layer halves the number of dangling bonds, lowering the total energy. Furthermore, the buckling of dimers (i.e., the tilted dimer bond) lowers the total energy by opening the gap between the occupied band associated with the dimer-up atom and the unoccupied band associated with the dimer-down atom. The properties of Si(100) and Ge(100) and their building blocks can be modified by the adsorption of metal atoms. An understanding of the mechanisms behind such modifications is important from both fundamental and technological viewpoints, providing the groundwork for surface and interface engineering. For example, a 1/2 monolayer (ML) of Sr atoms on Si(100) produces the (1×2) reconstruction with saturated dangling bonds, which can serve as a template for growing the crystalline high-k oxides on silicon that are a novel promising material for metal-oxide-semiconductor field-effect transistors (Ref. 1 and references therein).

Several reconstructions with $(2 \times n)$ periodicities (n = 3, 4, 6, 7, 8) have been reported for rare earth (RE) metals on Si(100).^{2–15} Among those, the (2×3) form can be produced by RE adsorbates with different valence states, namely, divalent Yb^{6,7,12} and Eu (Ref. 9), trivalent Nd,⁶ and Sm,^{4,11,14} which can exhibit an intermediate valence on Si(100) (Refs. 16 and 17). Furthermore, this reconstruction has been found for alkaline earth metals as well.^{18–21} Thus, the (2×3) form can be consid-

ered as a prototype structure of metal/silicon (100) interfaces. In earlier studies, this structure was extensively probed with scanning tunneling microscopy (STM), which showed a strong influence of the electronic structure on the surface topography observed.^{4,6,7,9} Hence, structural models proposed for RE/Si(100)(2 × 3) have been tentative; that is, mostly atomic diagrams based on the registry of STM protrusions atop the intact Si(100)(2 × 1) backbone have been suggested.

More recently, the atomic geometry of (2×3) reconstructions has been examined by *ab initio* calculations for RE and Ba.²² A plausible model of the (2×3) unit cell with two metal atoms (i.e., 1/3 ML coverage) is found to include three silicon dimers, with one of them being buckled for the divalent adsorbates and none of them being buckled for the trivalent adsorbates. Therefore, a common concept can emerge from these findings: the symmetrization of silicon dimers requires a donation of two electrons from the metal to the surface per dimer. Indeed, this concept has been recently supported in a study of the (2×6) reconstruction formed by 1/2 ML Yb on Si(100).²³

In this work, we shed more light on the structural and electronic properties of RE/Si(100)(2 \times 3) by exploring Sm-induced reconstruction by means of high-resolution photoelectron spectroscopy using synchrotron radiation and density functional theory (DFT) calculations. Samarium can change valence depending on the surrounding atoms, and, consequently, the Sm/Si(100) surface represents a good platform to examine the above concept for Si dimer–containing reconstructions. Based on STM, Ragan *et al.* proposed a schematic of the Sm/Si(100)(2 \times 3) structure including two metal atoms in the unit cell.⁴ Ohbuchi and Nogami reported

two different Sm/Si(100)(2 \times 3) reconstructions, one that includes two metal atoms and another that has a different Sm coverage.¹¹ The theoretical study in Ref. 22 constructed a favorable model of $Sm/Si(100)(2 \times 3)$ in the case of trivalent Sm atoms. However, the valence of Sm in the (2×3) reconstruction is still unknown. Here we measured Sm 4f emission to unveil it, which allows us to propose a plausible atomic structure of $Sm/Si(100)(2 \times 3)$ on the basis of DFT. Si 2p core-level photoemission is applied to probe the detailed atomic arrangement of Si substrate through careful quantitative line shape analysis, taking advantage of improved energy resolution. This technique is very sensitive to charge redistribution between the up and down atoms of the buckled silicon dimer, and it is sufficiently rapid for probing of buckled dimers in flip-flop motion, in contrast to STM. Surface core-level shifts (SCLSs) measured by Si 2p spectroscopy are interpreted on the basis of DFT calculations performed for different structural models. Finally, we put forward a hitherto unreported approach for RE/Si(100) to compare the measured and calculated SCLS data.

II. EXPERIMENTAL AND CALCULATIONAL DETAILS

The measurements were carried out on beamline I4 at the MAX-lab synchrotron radiation facility in Lund, Sweden. The Si samples were cut from P-doped (100) wafer (*n*-type, 1 Ω ·cm) and cleaned *in situ* using the standard procedure (Ref. 6). After the cleaning, sharp (2 × 1) and c(4 × 2) low-energy electron diffraction (LEED) patterns (not shown) were observed at 300 and 100 K, respectively. Samarium was deposited from a tungsten filament evaporator. The deposition rate was measured by a quartz crystal microbalance. The (2 × 3) reconstruction was produced by the deposition of 1/3 ML Sm (1 ML = 6.78×10^{14} cm⁻²) onto the clean Si(100) at 300 K, followed by annealing at 800 K. LEED displayed a sharp (2 × 3) pattern without any superimposed structures (Fig. 1). Sample heating was performed by direct current. The temperature was measured by an infrared pyrometer.



at 1/3 ML. The electron energy is 57 eV.

The photoelectron spectra were acquired at the normal emission angle with the SPECS Phoibos 100 analyzer at the sample temperature of 100 K. The acceptance cone of the analyzer was $\pm 8^{\circ}$. The Si 2*p* emission was measured in the photon energy range $125 \leq hv \leq 145$ eV, with total energy resolution of 56–66 meV, which was slightly dependent on hv. The valence spectra were taken at hv = 21.2 eV, with total energy resolution of 54 meV. Sm 4*f* emission was recorded at hv = 150 eV (the energy resolution is 110 meV). The binding energy was referred to the Fermi level position of a reference Ta sample in a good contact with the Si sample.

The calculations were performed by using the Vienna *ab* initio simulation package (VASP),²⁴ applying the projector augmented wave (PAW) method²⁵ and the local density approximation (LDA) of Ceperley and Alder,²⁶ as parameterized by Perdew and Zunger.²⁷ The atomic structure was optimized by using conjugate-gradient minimization of the total energy with respect to the atomic coordinates. The Sm 6s and 5p, and the Si 3s and 3p electrons were included as valence electrons. Two slabs were utilized. One of them consisted of one Sm layer and eleven Si layers, and the dangling bonds of the bottom surface Si atoms were passivated by hydrogen atoms (i.e., the hydrogenated slab). The other slab included 22 Si layers, and both of their surfaces were covered with adsorbed Sm atoms [i.e., the symmetrical (2×3) slab]. For the hydrogenated slab, two bottom Si layers were fixed to the ideal bulk positions. Other atoms, including the hydrogen atoms, were relaxed until the remaining forces were less than 20 meV/Å. Two Si lattice constant parameters, $a_{Si} = 3.8387$ and 3.8193 Å, were used. The latter value is the theoretical equilibrium LDA lattice parameter. The results (i.e., the fully optimized atomic configurations and SCLSs) were found to be very similar, demonstrating the same trends for both slabs and both lattice parameters. For this reason, we report here only the data obtained for the symmetrical slab and $a_{Si} = 3.8193$ Å, unless otherwise specified. The symmetrical slab is used because of possible uncertainty for the bulk reference potential in the complete screening model with the hydrogenated slab (Ref. 28). The energy cutoff was 280 eV. The number of kpoints in the Brillouin zone was 24, corresponding to a k mesh of $6 \times 4 \times 1$ for the (2×3) reconstruction.

The SCLSs within the initial state model were evaluated by using the average electrostatic potential at the core of the Si atoms,²⁹ which was obtained by placing a test charge with the norm 1 at each Si ion. The Si 2p electrons were treated as core electrons. The inclusion of the 3d electrons as valence electrons was tested as well, and the results were very similar; i.e., the difference in SCLS did not exceed a few meV between the two treatments. The bulk reference value was obtained by averaging from layers 5–8. In the complete screening calculations, a single core electron was excited from the core to the valence by generating the corresponding core-excited PAW potential,³⁰ and thus the screening by valence electrons only was included.

III. RESULTS AND DISCUSSION

A. Sm 4f emission

The valence state of Sm atoms can be identified in 4f spectra where divalent (Sm²⁺, final state $4f^5$) and trivalent



FIG. 2. Sm 4*f* spectrum from the (2×3) surface at 100 K. The photon energy is 150 eV. The binding-energy regions for the divalent and trivalent Sm are shown. The inset illustrates a comparison of Sm 4*f* and Yb 4*f* spectra for Sm/Si(100)(2 × 3) and Yb/Si(100)(2 × 6) reconstructions where the RE atoms are divalent.

(Sm³⁺, final state $4f^4$) configurations are well separated in binding energy. Sm²⁺ appears in the binding-energy region from the Fermi energy to ~4.5 eV, and Sm³⁺ appears in the region from ~5 to ~11 eV (Ref. 31 and references therein). Figure 2 shows a Sm 4*f* spectrum taken from the (2 × 3) reconstruction at hv = 150 eV. This photon energy is slightly higher than the 4d - 4f resonant photon energy for the Sm²⁺ and Sm³⁺ contributions (134.3 and 142.2 eV, respectively).³¹ The spectrum clearly demonstrates the presence of multiplet structure for divalent Sm and the lack of emission from Sm³⁺. Therefore, we conclude that the samarium atoms in the (2 × 3) reconstruction are completely divalent.

We mention in passing that the divalent line shape in Fig. 2 is somewhat different from those of metallic Sm or its bulk compounds (e.g., Refs. 31-33). The intensity of the ⁶H subpeak at the binding energy of 0.9 eV appears to be much higher than those of ⁶F and ⁶P subpeaks at 1.7 and 3.9 eV, respectively. Moreover, the Sm 4f spectrum in Fig. 2 shows an additional feature at 2.45 eV that was not predicted in calculations (Ref. 34), but was identified for Sm compounds in experiments (Ref. 35). The origin of this feature is still unclear; however, it is unlikely that it is caused by contaminations.³⁵ Thus, we suggest that the enhanced intensity of the ⁶H subpeak in Sm 4 f emission is due to the specific environment of Sm atoms in the (2×3) reconstruction on Si(100). Note that ⁶H does not show any shoulder at 0.5 eV. Such a shoulder was found in the 4f emission from bulk metallic Sm, and it was assigned to the partial itinerant 4f electrons of the bulk Sm^{3+} (Ref. 36). In this study, the lack of this shoulder is well understood in terms of the absence of trivalent atoms, thus giving support to the above interpretation of this feature.

It is worth comparing 4f spectra for divalent RE atoms in Sm/Si(100)(2 × 3) and Yb/Si(100)(2 × 6) (Ref. 23) reconstructions. The comparison is shown in the inset of Fig. 2. It illustrates a difference in binding energy for the 4f level in



FIG. 3. Valence spectra for the clean Si and $\text{Sm/Si}(100)(2 \times 3)$ surfaces at 100 K. The photon energy is 21.2 eV. The arrow points to the characteristic feature that is due to the dangling bond state of the dimer-up atom on the clean surface.

Sm²⁺ and Yb²⁺. As seen, the Sm 4*f* electrons clearly have a lower binding energy as compared to the Yb 4*f* electrons. Therefore, the Sm²⁺ configuration is less stable than the Yb²⁺ configuration against the promotion of one 4*f* electron to the (6*s*5*d*) band and transition of RE atom to the trivalent $4f^{n-1}(6s5d)^3$ state. In the (2 × 3) reconstruction on Si(100), however, the divalent $4f^66s^2$ state of Sm atoms is favorable over the trivalent $4f^5(6s5d)^3$ one. The high stability of Yb²⁺ is explained by the fact that the 4*f* shell in the Yb atom is fully complete with 14 electrons.

B. Valence spectra

Figure 3 represents photoemission spectra from the valence band of clean substrate and $Sm/Si(100)(2 \times 3)$ reconstruction. Sm 4*f* emission does not contribute to the line shape under these experimental conditions, and, therefore, the spectra illustrate the changes that occurred in the surface electronic structure. First, it should be mentioned that no emission appears around the Fermi level, indicating the band gap and the semiconducting character for both the surfaces.

Second, a characteristic surface state at 0.7 eV on the clean $c(4 \times 2)$ surface (denoted by arrow) disappears after the formation of the Sm-stabilized (2 × 3) reconstruction. This state is associated with the dangling bond of the up atom of the buckled dimer on the clean substrate.³⁷ The disappearance of this feature means that the clean $c(4 \times 2)$ structure is completely replaced by the metal-induced (2 × 3) phase, and that no intact silicon dimers retain on this surface. We will discuss the silicon dimers in more detail later.

C. Si 2p line shape

Si 2p spectra measured for the Sm/Si(100)(2 × 3) reconstruction at various photon energies (the data points are illustrated by circles) are shown in Fig. 4. The spectra



FIG. 4. (Color online) Normalized Si 2p spectra of Sm/Si(100)(2 × 3) taken with various photon energies at 100 K and their decomposition. The experimental data are shown by circles. The resultant fitting curves and residuals are shown by solid lines. The shadowed spin-orbit doublets represent the Si 2p components of the spectra. The background was removed by the Shirley method. The residuals are multiplied by factor of 3.

are normalized to their maxima and given after background subtraction by the Shirley method. The fitting results are also represented in Fig. 4. The solid lines indicate the resultant fitting curves and residuals (multiplied by factor of 3). The shadowed doublets below each spectrum represent spin-orbitsplit components found from the line shape analysis. The spectral decomposition was performed by using a standard least-squares-fitting procedure with a linear combination of Voigt model functions. Several constraints, which are justified by the analysis of Si 2p line shapes for the clean substrate (not shown) and related RE/Si(100) surfaces (Refs. 9, 12, and 23), were exploited. In particular, the Lorentzian width (LW) and spin orbit splitting were kept constant for all components in all spectra. They were, respectively, 67 and 610 meV. The branching ratio was also constrained but allowed to slightly vary around the theoretical value for the 2p level (0.5) within 10% due to the possible diffraction effects. The Gaussian width (GW), binding energy (i.e., SCLS), and intensity of components were variable parameters. It was taken into account, however, that the SCLS of each component should not be affected by the photon energy. The GW is affected by the instrumental resolution, and, therefore, it should slightly increase with hv due to variation in total energy resolution. The SCLSs are given with respect to the bulk emission for which the relative binding energy is set to be 0 eV.

As a result of the improved high-energy resolution (56-66 meV) used in this study, the Si 2p line shape analysis required a careful fitting approach. In particular, the GW of a single component that originates from similar atoms should be relatively small ($\leq 200 \text{ meV}$) in such Si 2p measurements. For example, in our previous study with the same experimental setup, the bulk emission from the clean $Si(100)c(4 \times 2)$ was found to have a GW of 175 meV, and those of the first-layer and second-layer surface atoms were 188-203 meV, with a total energy resolution of 75 meV.²³ In this study, an initial fitting scheme included a bulk component (B) and three surface components. This fitting was clearly inconsistent, because the spectra could not be reproduced well, and SCLSs of surface components were strongly dependent on the photon energy. Moreover, the GWs of components were too large as compared to those of Refs. 23 and 38. This implies that the components used in this fitting scheme actually include hidden contributions, and, therefore, the number of surface components should be increased.

Next, various fitting schemes with four and five surface components were tested out. Again, all these schemes did not allow us to reproduce the Si 2p spectra reasonably. In the fitting scheme with four surface components, the lowest binding-energy spin-orbit doublet of which the $2p_{3/2}$ subpeak strongly contributes to the shoulder of the Si 2p spectra at -0.4 eV was found to have a GW of 320 meV or more, which clearly suggests the presence of two (or more) inequivalent Si atoms with slightly different core-level binding energies. In this scheme, GWs of other components, e.g., the bulk emission, were also clearly much larger than 200 meV. Finally, even with freely variable GW parameters, it was impossible to keep SCLSs independent of the photon energy. Therefore, we rule out the fitting scheme with four surface components.

In the fitting scheme with five surface components, of which three are shifted to the lower binding energy (i.e., the lowest binding-energy doublet is split into two separate SCLS doublets) and two are shifted to the higher binding energy relative to the bulk core level, the higher-binding-energy region of the Si 2p spectra could not be fitted reasonably without significant variation in SCLS of surface components or/and an increase in GW of the bulk component. As described below, this component includes a hidden contribution from subsurface atoms of which binding energies are slightly different from that of the true bulk atoms. The emission intensity ratio of such subsurface and bulk atoms is dependent on the photon energy, and, therefore, the respective single Voigt component would have an asymmetry, the degree of which depends on the experimental condition. Partially, this asymmetry can be compensated by the variation in SCLS of the higher-bindingenergy components; however, this makes the fitting with five surface components unsatisfactory as well.

Thus, a sixth surface component was introduced eventually. This fitting scheme was able to reproduce the spectra in Fig. 4 adequately, and we therefore conclude that there are at least six surface-shifted contributions to the Si 2p spectra from the Sm/Si(100)(2 × 3) reconstruction. In Fig. 4, these contributions are labeled S_{11} , S_{12} , S_2 , S_{SS} , S_3 , and S_4 , and their SCLSs are -0.46, -0.38, -0.17, 0.04, 0.16, and 0.34 eV,

respectively. The GW of *B* is 168 meV (at hv = 135 eV), and those of S_{11} , S_{12} , S_2 , S_{SS} , S_3 , and S_4 are 268, 187, 263, 178, 211, and 216 meV, respectively. The obtained GW values are in a good agreement with previous studies (Refs. 23 and 38). The intensity ratios of S_{11}/B , S_{12}/B , S_2/B , S_{SS}/B , S_3/B , and S_4/B increase at hv = 135 eV, which is a more surface sensitive condition, as compared to such ratios at hv = 125and 145 eV, which are more bulk sensitive conditions. This supports the bulk origin of *B* and the surface origin of S_{11} , S_{12} , S_2 , S_{SS} , S_3 , and S_4 .

It is worthwhile to compare the above SCLS data for the Sm/Si(100)(2 \times 3) reconstruction with those of similar Eu- and Yb-induced reconstructions in Refs. 9 and 12. The Eu/Si(100)(2 \times 3) reconstruction causes two surface-shifted components with negative SCLSs [S_1 (-0.54 eV) and S_2 (-0.24 eV) and two components with positive SCLSs [S₃ (0.21 eV) and $S_4 (0.51 \text{ eV})$.⁹ Similar surface components were found in the case of Yb (-0.43, -0.13, 0.21, and 0.39 eV).¹² In this study, the number of surface components is larger than those of Eu and Yb. Nevertheless, it can be seen that the core-level data show similar trends for all the systems. In particular, $Sm/Si(100)(2 \times 3)$ shows two well-resolved surface-related emissions shifted toward the higher binding energy relative to the bulk [i.e., S_3 (0.16 eV) and S_4 (0.34 eV)] and another one shifted toward the lower binding energy $[S_2 (-0.17 \text{ eV})]$. Each of them clearly has a one-to-one correspondence in the cases of Eu and Yb.

The lowest binding-energy surface-related component S_1 found for Eu and Yb in Refs. 9 and 12 is believed to be split into two components S_{11} (-0.46 eV) and S_{12} (-0.38 eV) in the present study of Sm. We assume that resolving S_{11} and S_{12} is due to the improved resolution, as remarked earlier. As also noted earlier, the splitting of a single component S_1 into S_{11} and S_{12} is required to fit the lowest binding-energy region of Si 2p spectra of Sm/Si(100)(2 × 3). S_{11} and S_{12} are sufficiently well separated in energy ($\sim 80 \text{ meV}$) to be resolved in the present study. The binding-energy difference of S_{SS} and B is twice as small as that of S_{11} and S_{12} (~40 meV); however, the introduction of S_{SS} is crucial to keep a reasonable GW of B and to avoid the variation in SCLS of S_3 and S_4 with changing photon energy. Most likely, the S_{SS} was unresolved and convoluted with the bulk emission in Refs. 9 and 12. Irrespective of the origin of this component, the presence of S_{SS} does not affect the main conclusions in this study. It should be also emphasized that both the S_{SS} component and the binding-energy splitting of S_{11} and S_{12} might not be revealed with poorer resolution; however, it is necessary to reproduce, respectively, the higher- and lower-binding-energy sides of the Si 2*p* spectra shown in Fig. 4 in this study.

It is noticeable that the GWs of S_{11} and S_{12} are significantly different (268 and 187 meV, respectively). The GW of S_{12} is very similar to that of the bulk emission (168 meV). Therefore, we suggest that the S_{12} has a single atom origin, i.e., the S_{12} is contributed by silicon atoms having identical bonding sites. In contrast, the S_{11} is assumed to have a multi-atomic origin, i.e., it stems from slightly different Si atoms at nonequivalent bonding sites, which accounts for the extra broadening of this component. Thus, at least three different Si atoms can contribute to the Si 2p spectra of Sm/Si(100)(2 × 3) in the lowest binding-energy region. Note that this region can be fitted very accurately, because the $2p_{3/2}$ peaks of the S_{11} and S_{12} spin-orbit doublets do not overlap with the other components significantly. The presence of S_{11} and S_{12} leads to a shoulder with specific line shape and extended tail in the spectra around the relative binding energy of -0.4 eV. Further, we will show that this shoulder is the fingerprint of the atomic geometry of the first Si layer with a buckled dimer.

D. Atomic model

When constructing a model of the Sm/Si (2×3) interface, the proposed structure is expected to meet certain conditions arising from the experimental findings in Sec. III A-III C. This prerequisite limits the amount of structures that should be examined by DFT. For instance, we do not consider here the atomic models where Sm atoms are trivalent²² or have a mixed valence, since the Sm atoms are completely divalent at the (2×3) surface, as shown in Sec. III A. Likewise, we discard the (2×3) models where the Sm coverage is different from 1/3 ML, since our LEED observations and coverage measurements support the scenario where the (2×3) unit cell does involve two Sm atoms, in good agreement with Refs. 4 and 14. This implies that Sm can donate four electrons to the (2×3) unit cell. Finally, we emphasize the nonmetallic electronic structure of $Sm/Si(100)(2 \times 3)$, as found in Sec. III B. This agrees with the fact that the unit cell of this surface contains an even number of silicon atoms with dangling bonds and the even number of electrons from the metal can interact with the dangling bond states.

Recently, the atomic geometry of Si(100)(2 \times 3) reconstructions with divalent Yb, Eu, and Ba adsorbates has been studied by DFT.²² This study has revealed that the favorable site for the metal atom in the fully relaxed structure is the valley bridge (T₃) site. The first-layer atoms of Si substrate tend to pairing (i.e., dimerization), and two plausible atomic models with different silicon-dimer patterns are possible. The (2×3) -II model has a more symmetrical dimer pattern, where the dimers form rows that are perfectly aligned along the [0-11] direction. The (2×3) -I structure has a more asymmetric pattern, where the perfect dimer rows are broken by a shift of every third dimer by a_{Si} in the direction perpendicular to the rows. Furthermore, among three silicon dimers in the (2×3) unit cell, one is much more tilted than the others (hereafter, we will call such dimers buckled and unbuckled, respectively). The calculations in Ref. 22 showed that the (2×3) -II structure is slightly more favorable than the (2×3) -I structure from the energetic viewpoint. As the Si dimers and T₃ adsorption site are key structural elements of these reconstructions, we call them "dimer-T₃" reconstructions.

In this study, the structural optimization of $Sm/Si(100)(2 \times 3)$ was performed for the initial atomic geometry where the first-layer Si atoms were slightly moved from their equilibrium bulk positions to allow their pairing; however, the buckling was removed in this atomic configuration. After the full optimization, it was found that the (2 × 3)-II form is favorable for Sm/Si(100) as well, and that the energy difference of (2 × 3)-II and (2 × 3)-I is 0.023 eV/(1 × 1). Similar to Yb, Eu, and Ba, the favorable site for the Sm atoms is T₃. One of three dimers in the (2 × 3) unit cell is much more buckled than the others. The favorable



FIG. 5. (Color online) Atomic model of the dimer- T_3 reconstruction of Sm/Si(100)(2 × 3). The Sm atoms and Si atoms in the first and second atomic layers are specified. The (2 × 3) unit cell is outlined.

"dimer-T₃" structure is shown in Fig. 5. The atomic positions of two Sm atoms are not completely identical. One of them is slightly above the other (by 0.03 Å). In Fig. 5, these atoms are labeled Sm_U and Sm_D, respectively. The lateral distance between Sm_U and Sm_D is 4.01 Å, which is higher than a_{Si} . The nonequivalence of Sm atoms is consistent with the brightness contrast of two STM protrusions for the Sm/Si(100)(2 × 3) reconstruction reported in Refs. 11 and 14. The vertical distance between the up and down atoms of the buckled Si dimer [the Si(E1) and Si(F1) atoms in Fig. 5] is 0.56 Å. The tilt of the other dimers, Si(A1)-Si(B1) and Si(C1)-Si(D1), is 0.02 and 0.06 Å, that is, these dimers are almost symmetrical. The second atomic layer shows a minor structural distortion (within 0.2 Å) in the [100] direction.

It is worthwhile noting that the favorable structural model obtained for the Sm/Si(100)(2 \times 3) reconstruction in this

study strongly resembles that of the $Y/Si(100)(2 \times 3)$ surface proposed in Ref. 14. First, similar adsorption sites are found for the metal atoms in the two models. Second, the dimerization of Si atoms is revealed in the first atomic layer. The (2×3) model for divalent Sm in this study includes one buckled Si dimer, whereas no buckled Si dimers were found for the (2×3) model of trivalent Y in Ref. 14. This difference will be well understood and explained in Sec. III F. Finally, a repulsive Coulomb interaction and tensile strain, leading to slight distortion of the metal adatom layer [i.e., two slightly different sites for the metal atoms in the (2×3) unit], are found. It is assumed that the lateral repulsion is due to the bonding mechanism for the adatoms, involving the strong charge transfer from the metal to silicon, as shown in Ref. 14. It is believed that this leads to the strong rearrangement of the first atomic layer of Si substrate and the dimer buckling found in the case of divalent Sm. Later herein, we will demonstrate the way in which such a rearrangement affects the Si 2p line shape measured for the Sm/Si(100)(2 \times 3) reconstruction.

E. DFT SCLSs

Table I represents SCLSs calculated within the initial state and complete screening models for the silicon atoms in the first four atomic layers of the dimer-T₃ structure in Fig. 5. The relaxation effect in the complete screening model, Δ_R , is defined as the difference between the complete screening and initial state SCLSs for each atom. Also, a similar set of data was obtained for a metastable, fully relaxed, (2 × 3)-II atomic configuration where the silicon dimers were unbuckled. Although this structure is less favorable energetically than the (2 × 3)-II structure with a buckled dimer in Fig. 5 [the energy difference is 16.5 meV/(1 × 1) surface area], it is important to compare the SCLS data for both structures in order to understand in detail the way in which the dimer buckling can

TABLE I. SCLSs calculated in the initial state and complete screening models and the relaxation shift for the Si atoms in the first four layers of the buckled (2 × 3)-II structure (Fig. 5). The relaxation shift (Δ_R) is defined as the difference of the complete screening and initial state SCLS values for each atom. The column "SCLS range" represents the differences between the largest and smallest SCLS values within each layer. The data are given in eV.

Layer	А	В	С	D	Е	F	SCLS range
			Initi	al state model			
1	-0.11	-0.18	-0.39	-0.54	0.52	-0.27	1.06
2	0.22	0.10	-0.08	-0.09	0.13	-0.09	0.31
3	0.04	0.36	-0.17	0.24	-0.04	0.21	0.53
4	-0.20	0.16	-0.17	0.12	-0.11	0.18	0.38
			Complet	e screening model			
1	-0.37	-0.43	-0.68	-0.73	-0.37	-0.68	0.36
2	-0.04	-0.20	-0.26	-0.26	-0.14	-0.33	0.22
3	-0.20	0.19	-0.32	0.15	-0.34	0.11	0.53
4	-0.34	0.07	-0.33	0.04	-0.20	0.11	0.45
			Relax	ation shift (Δ_R)			
1	-0.26	-0.25	-0.29	-0.19	-0.89	-0.41	
2	-0.26	-0.30	-0.18	-0.17	-0.27	-0.24	
3	-0.24	-0.17	-0.15	-0.09	-0.30	-0.10	
4	-0.14	-0.09	-0.16	-0.08	-0.09	-0.07	

Layer	А	В	С	D	Е	F	SCLS range
			Initi	al state model			
1	-0.19	-0.19	-0.24	-0.24	-0.24	-0.24	0.05
2	0.04	0.04	0.05	0.05	0.01	0.01	0.04
3	-0.11	0.31	-0.11	0.31	-0.06	0.21	0.42
4	-0.28	0.20	-0.18	0.15	-0.18	0.15	0.48
			Complet	te screening mode	1		
1	-0.46	-0.45	-0.86	-0.86	-0.86	-0.86	0.41
2	-0.26	-0.26	-0.26	-0.26	-0.34	-0.34	0.08
3	-0.34	0.12	-0.34	0.12	-0.42	0.05	0.54
4	-0.43	0.03	-0.31	0.03	-0.31	0.03	0.46
			Relax	ation shift (Δ_R)			
1	-0.27	-0.26	-0.62	-0.62	-0.62	-0.62	
2	-0.30	-0.30	-0.31	-0.31	-0.35	-0.35	
3	-0.23	-0.19	-0.23	-0.19	-0.36	-0.16	
4	-0.15	-0.17	-0.13	-0.12	-0.13	-0.12	

TABLE II. The same as in Table I but for the unbuckled (2×3) -II structure.

affect the core-level line shape. The initial state and complete screening SCLSs and Δ_R values for the unbuckled (2 × 3)-II structure are represented in Table II.

Within the initial state model, the buckled and unbuckled (2×3) -II structures show very similar trends for the third and fourth atomic layers but rather different trends for the first two layers, especially for the topmost layer. The total core-level binding-energy splitting for the topmost-layer atoms in the buckled structure (i.e., the SCLS range defined as a difference of the largest and smallest SCLSs) is as large as 1.06 eV. This suggests significant charge redistribution, not only for the buckled-dimer atoms E1 and F1 but also for the rest of the first-layer atoms in Fig. 5, e.g., the Si(D1) atom showing the most negative initial state SCLS (-0.54 eV). In other words, the interaction with the Sm_U and Sm_D atoms and the charge transfer from the metal to the substrate cause the strong rearrangement in the first Si layer, leaving one dimer buckled and the other two unbuckled. It is also possible that the charge redistribution for the Si(E1) and Si(F1) atoms of the buckled dimer affects the charge state of other first-layer atoms effectively, leading to the significant difference in SCLS for the first atomic layer. Obviously, this variation in SCLS makes the Si 2p line shape more complicated and can result in broadening of the spectra.

In contrast, the core-level binding-energy difference for the first-layer atoms in the unbuckled structure is as small as 0.05 eV, and the initial-state SCLSs of these atoms are found in the range of -0.24 to -0.19 eV. This implies that the specific bonding of Sm atoms in the unbuckled model and the absence of buckling lead to a more uniform distribution of electron charge within the first Si layer. Therefore, a more compact (narrower) Si 2p photoemission line can be predicted for such a structure.

When the complete screening effect is introduced, the DFT SCLSs for both atomic structures move to the lower binding energy systematically, which is a well-known trend found previously (e.g., Ref. 39). The relaxation shift Δ_R , however, is not the same for different atoms. It is most significant for

the first-layer atoms and gradually attenuates with increasing number of the atomic layer. The most efficient screening for the first-layer atoms can originate from the presence of unoccupied surface state bands due to the dangling bonds of such atoms. When the core is ionized, these bands can pull down below the Fermi level and become occupied, resulting in the strongest screening in the final state. Thus, the calculations predict that the final state effects are more prominent for the topmost-layer atoms and less significant for the atomic layers beneath the top layer in the Sm/Si(100)(2 × 3) reconstruction.

F. Si 2p core: Theory and experiment

The analysis in Sec. III E evidences that interpreting the atomic origins of measured SCLSs for Sm/Si(100)(2 × 3) is a rather complicated problem. First, the number of calculated SCLSs is much larger than the number of measured SCLSs in spite of resolving the novel components (S_{11} , S_{12} , and S_{SS}). This supports the above determination that the measured spectra include at least six surface components. However, it is reasonable to rationalize only the main trends in Si 2p photoemission from the Sm/Si(100)(2 × 3) and discuss origin of characteristic surface contributions to Si 2p spectra.

Second, the DFT calculations performed within the initial state and complete screening models can, respectively, underestimate and overestimate the kinetic energy of emitted electrons (i.e., the effect of shifting a calculated SCLS value toward the lower binding energy). In reality, however, a partial screening can occur, and, moreover, the degree of this screening can vary for different atoms. The situation is even more complicated, because the screening charge can effectively contribute to the kinetic energy of the emitted electron only in case that the response to the creation of photoionized core hole is fast enough, which depends on the properties of material and the electronic structure of the individual reconstruction.

We revealed that the use of either the initial state or complete screening model to interpret the core-level data is questionable in this study. For this reason, we propose a previously not reported approach based on combined initial state and complete screening theory. We found that the initial state theory is able to explain the SCLSs for the silicon atoms in the second, third, and fourth layers quite reasonably. This is well understood, because the relaxation shift $\Delta_{\rm R}$ is not very significant for such atoms, as shown in Sec. III E. Moreover, the initial state model can be applicable for related and other elemental semiconductor surfaces (e.g., Refs. 12, 23, and 38). However, it is questionable whether or not only the initial state can be applicable to interpret the SCLSs for the first-layer atoms in the Sm/Si(100)(2 \times 3) reconstruction, since the relaxation effects play a more significant role for these atoms (Sec. III E). Therefore, we consider the upper and lower limits for the SCLSs of such atoms, which are assumed to be the SCLSs calculated within the initial state and complete screening models, respectively. Thus, our interpretation of Si 2p line shape is based on the initial state core-level data calculated for the second-layer and deeper Si atoms and the combined initial state and complete screening data calculated for the first-layer atoms.

Figure 6 represents a schematic diagram illustrating the above comparison of measured and calculated core-level data. In the middle panel, the positions of measured surface and bulk components are shown by vertical bars, and the heights of these bars are proportional to the intensities of components. The positions of initial state SCLSs calculated for the atoms in the second, third, and fourth layers in the buckled and unbuckled (2×3) -II structures are also shown by vertical bars are proportional to the numbers of these bars are proportional to the numbers of these bars are proportional to the numbers of the bars are proportional to the numbers of the bars are proportional to the numbers of respective atoms in the reconstruction unit



FIG. 6. Comparison of calculated and measured SCLSs. For other details, see the text.

cell. Finally, horizontal bars in another two panels represent the binding-energy intervals in which the combined initial state and complete screening theory predicts the SCLSs for the first-layer atoms in each of the two atomic structures.

The analysis of Fig. 6 reveals that the S_2 , S_{SS} , S_3 , and S_4 components can be almost perfectly explained on the basis of the initial state SCLSs for atomic layers 2-4 in the buckled (2×3) -II structure. The respective data for the unbuckled (2×3) -II structure also give a reasonable interpretation, except for the SCLS of -0.28 eV found for one fourth-layer atom. This similarity is not surprising, because the atomic structure beneath the topmost layer of Si atoms in the (2×3) reconstruction is not significantly affected by the dimer buckling in the topmost atomic layer, and the initial state model is a good approximation for subsurface atoms. It is, however, difficult to unambiguously categorize the atoms contributing to individual components S_2 , S_{SS} , S_3 , and S_4 . Most likely, S_4 is strongly contributed by some of the third-layer atoms, whereas S_2 and S_3 are contributed by atoms in the second, third, and fourth layers (Table I).

More interesting is the interpretation of S_{11} and S_{12} contributing to the lowest binding-energy region of Si 2p spectra. As pointed out in Sec. III C, these components are caused by at least three inequivalent Si atoms. Figure 6 reveals that only the first-layer atoms can contribute to S_{11} and S_{12} . Moreover, only the buckled (2 × 3)-II structure is consistent with these SCLSs, whereas the unbuckled structure has two inequivalent first-layer atoms and therefore cannot explain the Si 2p line shape. Thus, the buckled (2 × 3)-II geometry is not only an energetically favorable structure, but it is also well consistent with photoelectron spectroscopy measurements.

This structure causes six different SCLSs for the first-layer Si atoms, of which possible Si 2*p* binding-energy ranges are shown by horizontal bars in Fig. 6. It is seen that the atoms C1 and F1 can contribute to S_{11} or S_{12} , the atom D1 to only S_{11} , the atoms A1 and B1 to S_{12} or S_2 , and the atom E1 to any of components, except for the S_{11} . Thus, the components S_{11} and S_{12} are interpreted as originating from the first-layer atoms, of which core-level binding energies are split due to the dimer buckling in the (2 × 3)-II structure.

The above results for the $Sm/Si(100)(2 \times 3)$ surface raise the question why silicon dimers are buckled or unbuckled in this reconstruction. This issue is not restricted to only this system, because Si dimer-containing reconstructions are found also for other RE/Si(100) interfaces (Refs. 22 and 23). As mentioned in Sec. I, the symmetrization of Si dimer is assumed to occur when the adsorbed metal atom can donate two electrons to the surface per dimer. This rule is obeyed for $Sm/Si(100)(2 \times 3)$, where two Sm atoms can donate four electrons to the reconstruction unit cell, leading to two symmetrical Si dimers, while the other (third) dimer remains asymmetric (buckled). In other words, the buckling rule suggests that the Si atom dimer bond on Si(100) is tilted, unless it can gain two or more electrons donated by the adsorbate. Other examples of Si dimer-containing RE/Si(100) reconstructions that obey the above rule can be found in literature. In particular, the Eu/Si(100)(2 \times 3) and Yb/Si(100)(2 \times 3) surfaces with a 1/3 ML coverage are shown to involve one buckled dimer per unit cell, whereas those with a 1/6 ML coverage include two buckled dimers.²² The 1/3 ML (2 \times 3) reconstructions of trivalent Sm or Nd atoms [they can donate 6 electrons per (2×3)] in Ref. 22 involve exclusively unbuckled dimers. A similar behavior is also found for trivalent Y in Ref. 14. The (2×4) reconstruction of divalent Yb on Si(100) (the coverage is 3/8 ML) includes one buckled and three unbuckled dimers, since Yb can donate 6 electrons per 4 dimers in this unit cell.²² Furthermore, the (2×6) reconstruction of Yb/Si(100) involves 6 divalent ytterbium atoms and 5 silicon dimers.²³ All these dimers are symmetrical because the metal atoms can donate 12 electrons, i.e., more than two electrons per dimer. Finally, we notice the (2×1) and $c(4 \times 2)$ reconstructions of the clean silicon substrate exhibit only the buckled dimers, which agrees with the buckling rule as well. Thus, the buckling of silicon dimer on the Si(100) surface is favorable until the dimer is added by two valence electrons from a foreign atom.

IV. CONCLUSIONS

The structural and electronic properties of $Sm/Si(100)(2 \times 3)$ with a 1/3 ML coverage have been studied by high-resolution photoelectron spectroscopy and DFT calculations. The Sm 4*f* spectrum revealed the divalent state of the Sm atoms. The valence-band measurements showed the semiconducting electronic structure of the Sm/Si(100)(2 × 3) surface. The Si 2*p* spectra are found to include at least six surface-shifted contributions, among which the S_{11} , S_{12} , and S_{SS} components were not resolved

in previous studies of related RE/Si(100) reconstructions. The surface components are interpreted on the basis of DFT calculations. Based on these calculations, the favorable atomic geometry of Sm/Si(100)(2 \times 3) is the dimer-T₃ (2 \times 3)-II structure with a buckled dimer. Thus, the buckling of Si dimers is a general phenomenon occurring on many surfaces, and not just on the pure Si(100) surface. This is verified by using surface core-level shifts for the RE/Si(100). The SCLSs calculated for the dimer-T₃ (2 \times 3)-II structure clearly agree with the experimental Si 2p line shape. The interpretation of this line shape is made in terms of combined initial state and complete screening models, where the SCLSs for the Si atoms in the second, third, and fourth atomic layers are described within the initial state model and those of the first atomic layer are described within the SCLS ranges limited by the initial state and complete screening values.

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- ¹J. W. Reiner, A. M. Kolpak, Y. Segal, K. F. Garrity, S. Ismail-Beigi,
- C. H. Ahn, and F. J. Walker, Adv. Mater. 22, 2919 (2010).
- ²B. Z. Liu and J. Nogami, Surf. Sci. **488**, 399 (2001).
- ³C. Ohbuchi and J. Nogami, Phys. Rev. B **66**, 165323 (2002).
- ⁴R. Ragan, Y. Chen, D. A. A. Ohlberg, G. Medeiros-Ribeiro, and R. S. Williams, J. Cryst. Growth **251**, 657 (2003).
- ⁵B. Z. Liu and J. Nogami, Surf. Sci. **540**, 136 (2003).
- ⁶M. Kuzmin, R. E. Perälä, P. Laukkanen, R.-L. Vaara, M. A. Mittsev, and I. J. Väyrynen, Appl. Surf. Sci. **214**, 196 (2003).
- ⁷M. V. Katkov and J. Nogami, Surf. Sci. **524**, 129 (2003).
- ⁸J. Yang, Q. Cai, X.-D. Wang, and R. Koch, Surf. Sci. **526**, 291 (2003).
- ⁹M. Kuzmin, R. E. Perälä, P. Laukkanen, and I. J. Väyrynen, Phys. Rev. B **72**, 085343 (2005).
- ¹⁰B. C. Harrison, P. Ryan, and J. J. Boland, Surf. Sci. 582, 79 (2005).
- ¹¹C. Ohbuchi and J. Nogami, Surf. Sci. **579**, 157 (2005).
- ¹²M. Kuzmin, M. P. J. Punkkinen, P. Laukkanen, R. E. Perälä, M. Ahola-Tuomi, T. Balasubramanian, and I. J. Väyrynen, Phys. Rev. B 78, 045318 (2008).
- ¹³A. Pratt, C. Woffinden, C. Bonet, and S. Tear, Phys. Rev. B 78, 155430 (2008).
- ¹⁴A. Shinde, J. Cao, W. Ouyang, R. Wu, and R. Ragan, Phys. Lett. A 373, 3459 (2009).
- ¹⁵Y. Cui and J. Nogami, Surf. Sci. **605**, 2038 (2011).
- ¹⁶Å. Fäldt and H. P. Myers, Phys. Rev. B **33**, 1424 (1986).
- ¹⁷J. Onsgaard, M. Christiansen, F. Ørskov, and P. J. Godowski, Surf. Sci. 247, 208 (1991).

- ¹⁸W. C. Fan and A. Ignatiev, Surf. Sci. 253, 297 (1991).
- ¹⁹W. C. Fan, N. J. Wu, and A. Ignatiev, Phys. Rev. B **42**, 1254 (1990).
- ²⁰Y. Kawashima, H. Takabe, T. Ikeda, H. Itoh, and T. Ichinokawa, Surf. Sci. **319**, 165 (1994).
- ²¹Y. Cui and J. Nogami, Surf. Sci. **603**, 3072 (2009).
- ²²M. P. J. Punkkinen, M. Kuzmin, P. Laukkanen, R. E. Perälä, M. Ahola-Tuomi, J. Lång, M. Ropo, M. Pessa, I. J. Väyrynen, K. Kokko, B. Johansson, and L. Vitos, Phys. Rev. B **80**, 235307 (2009).
- ²³M. Kuzmin, M. P. J. Punkkinen, P. Laukkanen, R. E. Perälä, V. Tuominen, J. J. K. Lång, M. Ahola-Tuomi, J. Dahl, T. Balasubramanian, B. Johansson, L. Vitos, and I. J. Väyrynen, Phys. Rev. B **82**, 113302 (2010).
- ²⁴G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993); 49, 14251 (1994); G. Kresse and J. Furthmüller, Comput. Mat. Sci. 6, 15 (1996); Phys. Rev. B 54, 11169 (1996).
- ²⁵P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994); G. Kresse, and D. Joubert, *ibid.* **59**, 1758 (1999).
- ²⁶D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- ²⁷J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
- ²⁸M. P. J. Punkkinen, K. Kokko, L. Vitos, P. Laukkanen, E. Airiskallio, M. Ropo, M. Ahola-Tuomi, M. Kuzmin, I. J. Väyrynen, and B. Johansson, Phys. Rev. B **77**, 245302 (2008).
- ²⁹G. Kresse and J. Furthmüller, *Vienna ab initio Simulation Package, Users guide* (The University of Vienna, Vienna, Austria, 2007).

- ³⁰L. Köhler and G. Kresse, Phys. Rev. B **70**, 165405 (2004).
- ³¹P. Wang, J. F. Ni, H. N. Li, W. H. Zhang, and J. F. Zhu, Surf. Sci. **602**, 3728 (2008).
- ³²M. Campagna, E. Bucher, G. K. Wertheim, and L. D. Longinotti, Phys. Rev. Lett. **33**, 165 (1974).
- ³³A. Chainani, H. Kumigashira, T. Ito, T. Sato, T. Takahashi, T. Yokoya, T. Higuchi, T. Takeuchi, S. Shin, and N. K. Sato, Phys. Rev. B 65, 155201 (2002).
- ³⁴F. Gerken, A. S. Flodström, J. Barth, L. I. Johansson, and C. Kunz, Phys. Scr. **32**, 43 (1985).

- ³⁵J. W. Allen, L. I. Johansson, I. Lindau, and S. B. Hagstrom, Phys. Rev. B **21**, 1335 (1980).
- ³⁶P. Strange, A. Svane, W. M. Temmerman, Z. Szotek, and H. Winter, Nature **399**, 756 (1999).
- ³⁷L. S. O. Johansson, R. I. G. Uhrberg, P. Mårtensson, and G. V. Hansson, Phys. Rev. B **42**, 1305 (1990).
- ³⁸M. Kuzmin, M. J. P. Punkkinen, P. Laukkanen, J. J. K. Lång, J. Dahl, V. Tuominen, M. Tuominen, R. E. Perälä, T. Balasubramanian, J. Adell, B. Johansson, L. Vitos, K. Kokko, and I. J. Väyrynen, Phys. Rev. B 83, 245319 (2011).
- ³⁹E. Pehlke and M. Scheffler, Phys. Rev. Lett. **71**, 2338 (1993).