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Atomic structure of the Sb/Si(100)-(2×1) surface

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We have determined the atomic structure of the Sb-covered Si(100) surface in one-monolayer coverage using the pseudopotential density-functional total-energy calculation scheme. Within a symmetric dimer model, we find that the equilibrium Sb-Sb dimer bond length and Sb-Si back bond length are 2.94 and 2.59 Å, respectively, in good agreement with a surface-extended x-ray-absorption fine-structure measurement. In addition, the Si substrate recovers a bulklike geometry upon Sb adsorption: atomic displacements from the bulk positions are all within 0.03 Å. We explain a large difference in the experimental Si 2*p* core-level spectra for Sb/Si(100) and As/Si(100) in terms of the extent of substrate relaxations upon adsorption.

I. INTRODUCTION

A proper understanding of the adsorption geometry of group-V elements on the Si(100) substrate has been the objective of many experimental and theoretical studies[1-8] for its importance in improving the quality of III-V epitaxy on Si. The clean Si(100) surface has a dimerized (2×1) structure.[9] However, the adsorption of some group-V elements such as Sb (Refs. 1-5) and As (Refs. 6 and 7) on Si(100) is known to resolve the (2×1) reconstruction of the Si substrate: the adsorbed Sb (or As) atoms tend to form surface dimers with the Si substrate kept in near-bulk configurations.

For the Sb/Si(100) system, earlier x-ray photoemission spectroscopy (XPS) results by Rich *et al.*[1] showed that the Si core-level spectra exhibit a single bulklike component, i.e., the surface components due to the (2×1) reconstruction disappear after Sb adsorption. Recently, Richter *et al.*[2] verified from a combined surface-extended x-ray-absorption fine-structure (SEXAFS) and scanning-tunneling-microscopy (STM) study that Sb atoms dimerize on Si(100), and the corresponding Sb-Sb dimer bond length and Sb-Si back bond length are 2.88 and 2.63 Å, respectively. More recently, Slijkerman, Zagwijn, and van der Veen[3] investigated the morphology of the Sb overlayer and reordering of the Si substrate upon Sb adsorption using medium-energy ion scattering (MEIS). They reported that the Si(100) substrate recovers the bulk geometry underneath the Sb overlayer.

In spite of many experimental results for the atomic structure of the Sb/Si(100)-(2×1) surface,[1-4] there are few theoretical studies on this system.[5] Recently, Tang and Freeman[5] studied the structure of Sb dimers on Si(100) using the density-functional cluster calculation, but the details of the subsurface relaxation were not known. In the present paper, we investigate the atomic structure of the Sb/Si(100)-(2×1) surface at 1-ML Sb coverage by using the pseudopotential density-functional band calculation scheme. The main purpose of this paper is to discuss the differences in the XPS results between Sb/Si(100) and As/Si(100) by comparing both atomic structures on an equal ground. Based on the symmetric Sb-Sb dimer model,[1-5] we determine the equilibrium atomic geometry of the top four surface layers in a 12-layer slab representation by calculating the Hellmann-Feynman atomic forces. We find that the Sb-Sb dimer bond length and Sb-Si back bond length are 2.94 and 2.59 Å, respectively, in good agreement with the SEXAFS measurement.[2] In addition, unlike the case of As/Si(100)-(2×1), the calculated displacements of the substrate Si atoms in Sb/Si(100)-(2×1) from the ideal bulk positions are all within 0.03 Å; that is, the present theory confirms the MEIS result[3] that the Si(100) substrate restores a bulklike geometry upon Sb adsorption, and also provides a reasonable explanation for the experimental observation[1] that the Si 2*p* surface core-level components on Si(100)-(2×1) disappear after Sb adsorption.

The rest of the text is organized as follows. In Sec. II the calculational scheme is described. In Sec. III we determine the equilibrium atomic structure of the Sb/Si(100)-(2×1) surface and compare them with experiments. We also discuss the differences in the core-level photoemission results for the Sb/Si(100)-(2×1) and As/Si(100)-(2×1) surfaces. Finally, a summary is given in Sec. IV.

II. PSEUDOPOTENTIAL DENSITY-FUNCTIONAL TOTAL-ENERGY FORMALISM

We perform total-energy calculations using the pseudopotential density-functional total-energy scheme. Details on the scheme and on its previous applications to surfaces can be found in Refs. 10 and 11. We use the norm-conserving pseudopotentials of the Kleinman-Bylander type[12,13] and the Ceperley-Alder exchange-correlation energy functional in the local-density approximation.[14,15] The surface is simulated by a periodic slab geometry. The unit supercell contains 12 atomic layers and 4 vacuum layers. We use a plane-wave basis set with an energy cutoff of 10 Ry and take a uniform grid of 32 k points in the (2×1) Brillouin zone. The Sb and Si atoms on the top four layers are relaxed along the calculated Hellmann-Feynman forces until the magnitudes of the forces are less than 10 mRy/Å.

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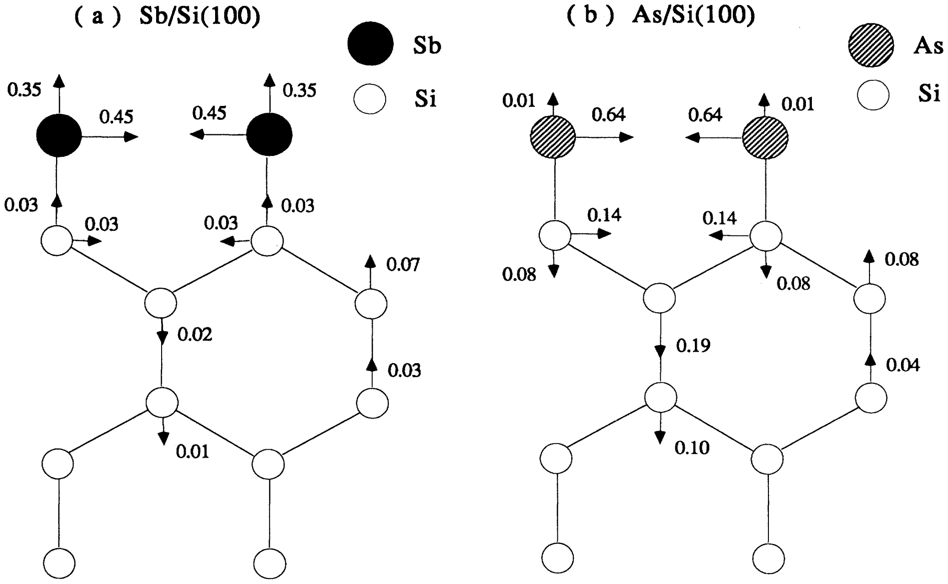

FIG. 1. Equilibrium atomic structures of the Sb/Si(100)-(2×1) and As/Si(100)-(2×1) surfaces. The bulk lattice constant of Si used is 5.43 Å and atomic displacements from the bulk positions are given in units of Å.

III. RESULTS

In order to optimize the atomic structure of the Sb/Si(100)-(2×1) surface, we take its initial atomic coordinates from our previous results for the symmetric dimer model of the clean Si(100) surface.[10] Based on a wide variety of experimental evidence,[1,2,4] we employ the symmetric Sb-Sb dimer model in the present paper. We first replace the top-layer Si dimers on Si(100) by Sb dimers, where the Sb-Sb and Sb-Si bond lengths are readjusted by using the sum of the covalent radii of Sb and Si. The atomic coordinates of the structure are then relaxed and the final structure obtained is shown in Fig. 1(a). We find that the calculated displacements of the substrate Si atoms from the bulk positions are at most about 0.07 Å. This recovery of the Si bulk geometry upon Sb adsorption is spectacular compared with the clean Si(100) surface where the atomic displacements of the second-layer Si atoms are about 0.1–0.2 Å.[10,16–18] The present result confirms the MEIS results of Slijkerman, Zagwijn, and van der Veen[3] that the Si substrate shows a bulklike structure after Sb adsorption.

TABLE I. Calculated dimer bond length (d_D) and back bond length (d_{12}) for the Sb/Si(100)-(2×1) and As/Si(100)-(2×1) surfaces in comparison with the previous theoretical and experimental results.

	d_D (Å)	d_{12} (Å)
Sb/Si(100)		
SEXAFS[a]	2.88	2.63
Previous theory (Tang and Freeman)[b]	2.93	2.61
Present theory	2.94	2.59
As/Si(100)		
X-ray diffraction[c]	2.55	
Previous theory (Uhrberg *et al.*)[d]	2.55	2.44
Present theory	2.57	2.45

[a] Reference 2.
[b] Reference 5.
[c] Reference 7.
[d] Reference 6.

In the equilibrium atomic structure of the Sb/Si(100)-(2×1) surface shown in Fig. 1(a), the Sb-Sb dimer bond length (d_D) and Sb-Si back bond length (d_{12}) are 2.94 and 2.59 Å, respectively. The present result is compared with previous studies in Table I. By using a combination of SEXAFS and STM, Richter *et al.*[2] determined the bonding geometry of the Sb/Si(100)-(2×1) surface. They reported that the Sb atoms form dimer rows that run perpendicular to the original Si dimer rows of the clean Si(100) surface, and the measured d_D and d_{12} are 2.88±0.03 and 2.63±0.04 Å, respectively. Recently, in their density-functional cluster calculations for the adsorption of Sb on Si(100)-(2×1), Tang and Freeman[5] obtained $d_D = 2.93$ and $d_{12} = 2.61$ Å. The agreement in bond lengths among theories and experiment is quite good.

Although Sb and As are the same group-V elements, there exists a noticeable difference in the core-level photoemission spectra for the Sb/Si(100)-(2×1) and As/Si(100)-(2×1) surfaces: while there remains a surface component for the Si $2p$ core levels (0.45 eV shifted from the bulk one) in As/Si(100),[8] Si $2p$ surface components disappear upon Sb adsorption.[1] Rich *et al.* have related this difference to the different electronegativities of Sb and As.[1] Partially ionic As-Si bondings (due to a larger electronegativity of As) make the subsurface Si atoms electronically differ from the bulk ones. On the other hand, the Sb adsorbates with a comparable electronegativity leave the subsurface Si atoms in near-bulk configuration. As a matter of fact, the surface core-level spectra in most cases reflect well the nature of chemical bondings or underlying atomic structures at the surface. It is thus of interest to compare the atomic structures of the Sb/Si(100)-(2×1) and As/Si(100)-(2×1) surfaces.

We determine the atomic structure of the As/Si(100)-(2×1) surface using the same structure model and computational parameters as the Sb/Si(100)-(2×1) case. The equilibrium surface structure is shown in Fig. 1(b). The calculated As-As dimer bond length and As-Si back bond length are found to be 2.57 and 2.45 Å, respectively. As in the case of the Sb/Si(100) system, the calculated bond lengths agree well with a previous theoretical calculation[6] and x-ray-diffraction measurement[7] (see Table I). In Fig. 1, we find that there is a large difference in the substrate relaxation between the Sb/Si(100)-(2×1) and As/Si(100)-(2×1) surfaces. Unlike Sb/Si(100), the calculated displacements of the substrate Si atoms in As/Si(100) are as large as about 0.1–0.2 Å. While a separation of Si 2*p* surface components is not probable in the bulklike tetrahedral bonding arrangement of the subsurface Si atoms in Sb/Si(100), noticeable surface core-level shifts are expected in As/Si(100) from the large relaxation of the subsurface Si atoms. Hence, the present determination of the surface structures provides a natural explanation for the difference found in the Si 2*p* core-level spectra on Sb/Si(100) (Ref. 1) and on As/Si(100) (Ref. 8).

IV. SUMMARY

In summary, we have determined the atomic structure of the Sb/Si(100)-(2×1) surface by using the pseudopotential density-functional total-energy calculation scheme. The equilibrium Sb-Sb dimer bond length and Sb-Si back bond length are found to be 2.94 and 2.59 Å, respectively, in good agreement with the previous theoretical calculation and SEXAFS measurement. In addition, unlike the case of As/Si(100)-(2×1), the relaxation of the Si substrate in the Sb/Si(100)-(2×1) surface is negligible, resulting in a bulklike atomic environment for the Si atoms. We have explained the large difference in the observed photoemission core-level spectra for the Sb/Si(100) and As/Si(100) systems in terms of the extent of substrate relaxations upon adsorption.

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