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Ab initio calculations of surface structure and electronic properties caused by adsorption of Ca atoms on a Si(1 1 0) surface

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ABSTRACT

The adsorption of Ca metals onto a Si(1 1 0) surface has been theoretically investigated by first-principle total-energy calculations. We employed a local density approximation of the density functional theory as well as a pseudopotential theory to study the atomic and electronic properties of the Ca/Si(1 1 0) structure. The (1×1) and (2×1) surface structures were considered for Ca coverages of 0.5 and 0.25 ML, respectively. It is found that the (1×1) phase is not expected to occur even for rich Ca regime. It was found that Ca adatoms are adsorbed on top of the surface and form a bridge with the uppermost Si atoms. The most stable structure of Ca/Si(1 1 0)–(2×1) surface produces a semiconducting surface band structure with a direct band gap that is slightly smaller than that of the clean surface. We have observed one filled and two empty surface states in the gap region. These empty surface states originated from the uppermost Si dangling bond states and the Ca 4*s* states. Furthermore, the Ca–Si bonds have an ionic nature with almost complete charge transfer from Ca to the surface Si atoms. The structural parameters of the ground state atomic configuration are detailed and compared with the available results of metal-adsorbed Si(1 1 0) surface, Ca/Si(0 0 1), and Ca/Si(1 1 1) structures.

1. Introduction

Metallic adsorption on semiconductor surfaces has been the subject of an enormous number of experimental and theoretical investigations due to its possible technological and industrial applications. Based on metallic adsorption onto semiconductor surfaces there have been many experimental works devoted to fabricate nanoscale electronic devices using self-assembled one-dimensional (1D) overlayer structures. These 1D structures have received immense interest due to the possibility of various exotic physical phenomena such as formation of non-Fermi-liquid-like ground states, Peierls-like phase transitions, and order–disorder transitions, as well as the potential applications of these phenomena in nanotechnology [1–6]. Among the vast number of semiconductor materials, group-IV semiconductor surfaces (namely Si surfaces) are the keystones of most of the electronic devices and hence have been used in many different investigations. Apart from the most studied Si(1 0 0) and Si(1 1 1) surfaces for metallic adsorbates, there has been very little attention paid to the study of the adsorption of metallic atoms on the Si(1 1 0) surface. The main reason for this can be attributed to the experimental difficulties in preparing a clean Si(1 1 0) surface [7]. The difficulties in producing Si(1 1 0) have led Si(1 0 0) to be the most desired surface for microelectronics applications such as metal oxide semiconductor field effect transistors (MOSFETs). However, the Si(1 1 0) surface has recently been reinvestigated in an attempt to extend current fabrication technologies, not only because the existing MOSFET fabrication techniques are reaching fundamental physical limits, but also because the fabrication challenges for Si(1 1 0) including substrate planarization [8] and the growth of high-quality gate oxide layers [9] have been experimentally overcome. These technical developments suggest that Si(1 1 0) could be of great importance as a newly accessible surface for electronic applications. Therefore, the emphasis is now on the need for further investigations of industrially important processes such as metal deposition on the Si(1 1 0) surface. To date, the atomic structure of the (1 1 0) surface of Si has been the subject of some controversy. Despite many works that suggest various reconstructions for clean Si(1 1 0) surface including the (1×1), (2×1), (5×1), (7×1), (9×1), (4×5), (5×4), (16×2), and (32×2) phases, it has been reported that only a (16×2) reconstruction can exist in a pure form and that all the other various reconstructions must be temperature and dopant stabilized. However, this controversy suggests that there is no firm structural model for clean surface and/or metal-induced surface [10–20]. Recently, Sakamoto et al. [21] have investigated the electronic structure of a single domain Si(1 1 0)–(16×2) surface using high-resolution angle-resolved photoelectron spectroscopy (ARPES) and scanning tunneling microscopy (STM)

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measurements. Their ARPES spectra revealed four dispersive semiconducting surface states in the bulk band gap. With the help of STM analysis, these four states were found to originate from the adatom's dangling bonds, dangling bonds of the upper atoms of the buckled Si, dangling bonds of both the lower buckled Si atoms and the first layer of unbuckled Si atoms, and dangling bonds of the second layer of Si atoms. Moreover, they also observed six more surface states within the projected bulk band.

Different experimental [22–25] and theoretical [26,27] studies have been performed to investigate the adsorption of elements onto the Si(1 1 0) surface for different reconstructed unit cells. Experimentally, Rich et al. [16] showed that a single monolayer (ML) of Sb deposited onto a Si(1 1 0) surface held at temperatures between 320 and 370 °C forms a (2×3) structure. They used low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) techniques to demonstrate that the two different Sb-induced Si(1 1 0)–(2×3) reconstructions exist, and these reconstructions correspond to Sb coverage of 0.85–1.0 and 0.3–0.6 ML. Michel et al. [22] have used X-ray standing-wave fields (XSW) to investigate the adsorption of Cs onto a Si(1 1 0) surface. Their results showed that the hollow adsorption site is favored. It has also been reported that different Cs-induced surface reconstructions $(1\times1,\ 2\times2,$ and $5\times4)$ were observed after Cs deposition depending on the Cs coverage. However, at a saturation coverage of 0.5 ML, the surface displays a (1×1) LEED pattern. Decreasing the coverage to 0.15 ML leads to a (2×2) pattern, which becomes a (5×4) pattern at a coverage of 0.10 ML. Sakama and Kawazu [23] have performed quadrupole mass spectroscopy (QMS), AES, and LEED measurements to investigate the adsorption of Ga onto a Si(1 1 0) surface. Their results indicated three adsorption phases (α, β, and γ) that appear at a metal coverage of 0.11 and 0.17 ML for the α and β phases, respectively, whereas the γ phase is not saturated. The induced atomic structures upon the adsorption of Ag onto a Si(1 1 0) surface have been investigated by Maslova et al. [24] using STM. They found that the surface maintains the original (16×2) unit cell with up to 0.21 ML of Ag coverage. When the Ag coverage is increased to approximately 0.42 ML, the surface reconstruction changes from the (16×2) to the (4×1) structure. Recently, Kang et al. [25] have explored the phase formation and electronic properties of Au-induced reconstruction of the Si(1 1 0) surface as a function of the metal coverage using LEED and angle-resolved photoemission (ARP) measurements. While a well-ordered (1×2) LEED pattern is observed at a metallic coverage of approximately 0.20 ML, a well-defined (2×5) LEED pattern appears at a coverage of 0.4 ML, and these observations are consistent with the reflection high-energy electron diffraction (RHEED) measurements. The ARP measurements reveal no clear surface state bands on the (1×2) surface within the bulk band gap, whereas the (2×5) surface exhibits two dispersive metallic bands with exact quarter and half fillings. Theoretically, Menon et al. [26] have investigated the chemisorption of Si atoms onto the Si(1 1 0) surface within the framework of a tight-binding molecular-dynamics scheme incorporating Green's-function method. Their results support the rotational model for surface reconstructions of the $n\times1(n\geq1)$ type. They have also found that the (2×1) and (1×1) reconstructions are isoenergetic with no surface dimer formation. First-principle total-energy calculations of the Sb/Si(1 1 0)–(2×3) structure with 1/3, 1/2, and 1.0 ML coverages of Sb atoms have been performed by Takeuchi [27] following the experimental results obtained by Rich et al. [16]. Only the structures corresponding to the 1/3 and 1.0 ML coverages were found to be stable and these coverages were found to have adatom and trimer structures, respectively. Very recently, Huitzil-Tepanecatl et al. [28] have theoretically reproduced the results obtained by Takeuchi [27] for the Sb/Si(1 1 0)–(2×3) structure with 1/3 and 1.0 ML coverages of Sb atoms and presented *ab initio* calculations for a As/Si(1 1 0)-(2×3) phase that employed similar coverage percentages. In addition to their confirmative results for the Sb-induced surface compared with the work done by Takeuchi [27], their results for As adsorption show that for 1/3 ML (1.0 ML) coverage, tetrahedrons (microfacets) represent the most stable configuration. From above, we can clearly note that almost all the fundamental groups of the periodic table have been studied in terms of their adsorption onto a Si(1 1 0) surface, except for elements from group II (alkaline-earth metals; AEMs). To the best of our knowledge, there have been no experimental or theoretical investigations about the atomic adsorption of AEMs (Ca atoms are of particular interest) onto the Si(1 1 0) surface. Conversely, many research efforts have been undertaken to study Ca on Si(0 0 1) [29,30], and Si(1 1 1) surfaces [31–37].

To explore the structural and electronic properties of the Si(1 1 0) surface upon the adsorption of Ca atoms, we present in this paper first-principle density functional calculations. Among various structural models, (1×1) and (2×1) corresponding to 0.5 and 0.25 ML of Ca atoms, respectively, are studied. Our total-energy calculations of these structures suggest that the (1×1) conformation is not expected to appear. However, the optimized structure and electronic properties of the Ca/Si(1 1 0)–(2×1) surfaces are highlighted. The mechanism of charge transfer from the Ca adatom to the topmost Si surface atoms is detailed. Although experimental studies on the Ca/Si(1 1 0) surface have not yet been reported, the obtained results are compared with the available theoretical findings for the Ca/Si(0 0 1) and Ca/Si(1 1 1) structures and other metals adsorbed onto a Si(1 1 0) surface.

2. Computational framework

The local density approximation of the density functional theory [38] as implemented in the Quantum-ESPRESSO simulation package [39] was used to perform the present *ab initio* calculations. The Ceperley–Alder [40] form of the exchange-correlation energy, as parameterized by Perdew and Zunger [41], was used to describe the electron–electron interaction. Ion–electron interactions were treated using norm-conserving, *ab initio*, fully separable pseudopotentials [42,43] in the framework of the Bachelet, Hamann, and Schlüter scheme [44]. The single-particle Kohn–Sham [45] wave functions were expanded in a plane wave basis set with a kinetic-energy cutoff of 12 Ry, which is sufficient to obtain well-converged results. Throughout the calculations, we use the calculated Si equilibrium lattice constant of 5.43 Å, which is comparable to the reported experimental value.

For the surface calculations, we have adopted the repeated slab technique [46]; each slab consists of nine layers of Si atoms and a layer of Ca adatoms. To minimize the interactions between the two neighboring slabs along the normal direction, they were separated by a vacuum region equivalent to six times the lattice constant and the bottom layer was terminated by hydrogen atoms. The topmost seven Si layers of the slab and the Ca atoms were given full freedom to move while the last two bottom layers of Si were held fixed at ideal positions to simulate a bulk-like termination. No symmetry constraint is imposed on the atoms that are free to move. The Hellmann–Feynman forces on the ions were calculated and minimized to obtain a relaxed atomic geometry. Atoms were relaxed until forces converged to approximately 5 meV/Å. Self-consistent solutions of the Kohn–Sham equations were obtained by employing $2\times2\times1$ and $2\times4\times1$ k-point Monkhorst–Pack [47] sets within the surface Brillouin zones for the (1×1) and (2×1) structures, respectively. The number of layers, vacuum size, number of k points, and energy cutoff were carefully chosen after several convergence tests.