Electronic surface structure of CoSi$_2$(111)/Si(111): implications for ballistic electron-emission microscopy currents

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Abstract

Using a decimation technique, and imposing electrostatic self-consistency, we compute the surface electronic structure of various CoSi$_2$(111)/Si(111) phases. The projected band structures and LDOS indicate a richness of surface related features. For the (1×1)Co-rich termination excellent agreement with experimental data and a recent DFT investigation is obtained. Strongly localized surface states on the high chain atoms of the (2×1) Pandey-chain like reconstruction are identified as causing the experimentally observed surface topography induced contrast in Ballistic Electron Emission Microscopy (BEEM) images of such films. © 2000 Published by Elsevier Science B.V.

Keywords: Electronic surface structure; CoSi$_2$(111); Si(111)

1. Introduction and theory

The structural problem of growing epitaxial CoSi$_2$ on Si(111) under ultrahigh-vacuum (UHV) conditions has been extensively studied in recent years [1–6]. Many experimental efforts have been put in the measurement of the surface electronic structure [7,8] but little theoretical information is available helping to coordinate the wealth of data into a consistent framework.[9a,9b] This is particularly surprising, as the strongly covalent bonding between Co and Si causes interesting surface states and related features. Further, a direct comparison between the electronic structure of both stable (1×1) phases, which most likely affects subsequent epitaxial layers, might even provide a valuable contribution to film growth understanding. Of specific interest is a (2×1) surface reconstruction found to coexist with the (1×1) termination under highly Si-rich conditions, and in this paper we shall focus on the implications for Ballistic Electron Emission Microscopy (BEEM) experiments [10a,10b] caused by the (2×1) electronic surface structure.

Our theoretical approach is based on a Linear Combination of Atomic Orbitals (LCAO) Hamiltonian within the two-center approximation introduced by Slater and Koster [12]. The tight-binding parameters are taken from independent work by Sanguinetti et al. [13]. They include next-neighbour interaction within each and in between all three sublattices of the CoSi$_2$ CaF$_2$-like structure. The extended basis of
$sp^3$ for Si and $sp^3d^5$ orbitals for Co with the inclusion of $d$-$d$ hopping elements between the metal atoms, has proven to reproduce accurately the bulk band structure as obtained from ab-initio calculations [14a,14b], as well as the experimentally determined bulk elastic constants. As expected, the TB approximation becomes less accurate for the high energy conduction bands above $\approx 3.00$ eV, which will therefore mark a natural upper limit for all further investigations.

Due to their small lattice mismatch of only $\approx 1.2\%$ (300 K), CoSi$_2$ films can be grown epitaxially on Si(111) in the CaF$_2$ structure [1]. Two different $(1 \times 1)$ surface phases are found to exist, depending on the particular growth conditions [2a,2b]: the so-called Co-rich termination, and the so-called Si-rich termination. Both structures have been analysed in a recent quantitative LEED study [3], allowing us to implement their exact experimental geometry into our TB model. Additionally, Stalder et al. [16] have reported a $(2 \times 1)$ surface reconstruction coexisting with the Si-rich phase for ultrathin ($d < 45$ Å), strained films grown on Si(111). Their STM investigation revealed $(2 \times 1)$ chains perpendicular to the three $< 2\bar{1}1>$ directions on the surface with a total corrugation amplitude perpendicular to the chains of 1 Å when imaged with a sample bias of 50 mV.

Based on these STM observations, Stalder et al. [16] proposed a structural model in analogy to Pandey’s $\pi$-bonded chain model for the $(2 \times 1)$ reconstruction of Si(111) [17]. Lacking a precise structure analysis in this case, a simplified and symmetrized version of this model is used in the present study (cf. inset of Fig. 2): the top CoSi$_2$ trilayer has been left with bulk spacings, while the position of the Si chain atoms is determined, keeping the Si–Si bond lengths at the ideal 2.35 Å bulk value wherever possible. It is a well known fact that Si bonds are highly sensitive to absolute length changes, whereas bond angles seem to play only a minor part [19]. Following Ancilotto’s suggestion [18] $\pi$-bonds within the chains are, however, marked by a $\approx 7\%$ contraction (2.20 Å). The tilting of the high chain is chosen to be 0.50 Å as in the Si(111) case. The low chain atoms are positioned 0.60 Å below, resulting in a total corrugation between high and low chains of 1.10 Å in close correspondence to the experimental value. The high chain tilt causes an asymmetrical situation, since the bond lengths of the ‘high chain up’ and ‘high chain down’ atoms to the low chain are obviously different. A further lateral shift in $< 2\bar{1}1>$ direction seems a natural consequence, but has been neglected trying to keep the model as simple as possible. Hence, the resulting bond lengths to the low chain are 2.43 and 2.27 Å, which reproduce at least on average the bulk value. Finally, the low chain to bulk distance has been adjusted to achieve the ideal 2.35 Å distance to the top trilayer Si atom.

The electronic surface computations have been performed using Green’s functions of a semi-infinite crystal. The lateral periodicity of the problem allows to calculate the retarded Green’s function $G^R(E,k)$ of one isolated layer as a function of energy and lateral momentum $k$ inside the projected 2D surface Brillouin zone. Construction of the semi-infinite crystal is subsequently achieved with a decimation technique that iteratively doubles the size of an existing slab until its two surfaces are effectively decoupled [11,19]. This procedure results in the surface Green’s function $G^R_{\text{surf}}(k)$ of an ideally bulk terminated, semi-infinite crystal. The surface reconstructions are finally included by gluing another superlayer to the semi-infinite slab by direct application of Dyson’s equation. Since in the case of the $(2 \times 1)$ surface reconstruction the vectors $k$ and $k + G$ inside the $(1 \times 1)$ surface Brillouin zone are equivalent due to the new prevailing periodicity, non-diagonal coupling terms $H(k, k + G)$ in the LCAO Hamiltonian have additionally to be considered.

As the Slater–Koster parameters have been obtained through fits to the bulk band structure, they obviously cannot take into account effects due to the truncation of bonds at the surface. In principle, it would be necessary to perform a self-consistent calculation determining the new charge distribution, which in turn would allow the adjustment of new surface TB parameters. However, this problem can be significantly simplified by realizing that mainly, the diagonal part of the Hamiltonian matrix is affected by the corresponding Coulomb potential. Further, a very simple approximation to this potential based on a local charge neutrality argument has proven to already give quite accurate results [19,20]: for each layer in the surface an artificial dipole
Table 1
Surface dipole potential in eV for all surface layers

<table>
<thead>
<tr>
<th>P</th>
<th>(1×1) Co-rich</th>
<th>(1×1) Si-rich</th>
<th>(2×1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{Si(1)} )</td>
<td>–</td>
<td>–0.30</td>
<td>–0.90 (high chain)</td>
</tr>
<tr>
<td>( V_{Si(2)} )</td>
<td>–</td>
<td>–0.25</td>
<td>–0.50 (low chain)</td>
</tr>
<tr>
<td>( V_{Si(3)} )</td>
<td>–0.40</td>
<td>–0.10</td>
<td>–0.20</td>
</tr>
<tr>
<td>( V_{Co(4)} )</td>
<td>1.30</td>
<td>1.20</td>
<td>1.10</td>
</tr>
<tr>
<td>( V_{Si(5)} )</td>
<td>–0.70</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

potential is introduced, which value is chosen as to achieve the correct integrated number of states at the Fermi level for each atom, i.e. electrostatic charge neutrality at the surface. The fitted values of the potential, which rigidly shifts all intra-atomic matrix elements of the LCAO Hamiltonian of the corresponding layer, are displayed in Table 1 for all surface phases.

2. Results

The \((1\times1)\) Co-rich surface termination is the only phase for which an ab-initio investigation using ultrasoft pseudopotentials in the generalized gradient approximation has already been performed [9a,9b]. Our results reproduce well the ones obtained by density functional theory, bringing further confidence on the accuracy of the method (this comparison will be presented elsewhere). We have also investigated the Si-rich surface phase, that will also be described elsewhere as it is not crucial for the present work. Our concern in the present work are the implications of the electronic structure on BEEM data, primarily collected for the \((2\times1)\) reconstruction, on which we shall henceforth concentrate.

Since CoSi₂ is metallic, no absolute bulk band gap is observed around the Fermi level. As depicted in Fig. 1, a major pseudo gap along \(\bar{J}-\bar{K}\) is, however, still present. The sketched surface states and resonances arise dominantly in the high chain atoms, which surface state enhancement can also impressively be seen in the calculated LDOS of this surface (Fig. 2). Even though these states do not display such a strong anisotropic dispersion as in the case of Si(111)-(2×1), they still cover most of the energy region around the Fermi level. Despite the \(\pi\)-bonding Si atoms, the CoSi₂ surface should thus be metallic, which agrees with the experimental STS data taken by Stalder et al. [16].

As can be seen in Fig. 2, the unoccupied surface peak is split into states exclusively on the top high chain atom with slightly lower energy and states with higher energies primarily on the downward tilted high chain atom. The lower energy peak of 0.80 eV might correspond to the large peak seen in
STS spectroscopy at 0.50 eV [16], which had then tentatively been assigned to a contribution from bulk CoSi₂. This is, however, unlikely, since bulk CoSi₂ contributions are rather expected below $E_F$. A second smaller peak seen at $-0.50$ eV corresponds to an occupied bonding state of the complete Si bilayer determined at $-0.30$ eV. This good agreement with available experimental data is gratifying, but we would like to stress that all these conclusions should be seen in light of the idealized structure assumed for the $2 \times 1$, that should be confirmed by standard structural techniques.

We suggest the strong surface states located on the high chain atoms in the energy range 0.00–2.00 eV should be the reason for the surface-induced contrast observed in BEEM experiments on CoSi₂/Si(111) [10a,10b]. Although the BEEM image represents the interface topography, an anti-corrugation contrast had been observed corresponding to the $(2 \times 1)$ chains of the reconstructed surface. Electrons to be detected as BEEM current have to overcome the Schottky barrier of 0.66 eV formed at the epitaxial interface. Since tunnel electrons injected into the surface states of the high chains couple less to the bulk states than those electrons injected directly into bulk states, it is reasonable to assume that there is a somewhat decreased probability for them to enter the semiconductor. The strong localization of the surface states on the two high chain atoms becomes apparent from Fig. 3, where the LDOS at the $\overline{K}$, which is the most important one for BEEM current, is depicted. The three surface peaks at energies above the Fermi-level, corresponding to the three surface bands seen in Fig. 1, are all concentrated roughly three times more on either of the two high chain atoms than on the low chain atoms. In view of these results, a larger fraction of electrons is obviously injected into surface states when the STM tip is positioned on top of the high chains. Keeping in mind that the experiment is performed in the constant current mode, this leaves a smaller fraction of electrons injected into bulk channels and would finally lead to a diminished BEEM current, explaining the observed anti-corrugation. Although this effect cannot amount to drastic BEEM current changes between high and low chains, it still causes a 20% variation in our calculations [21], which is close to the 7% variation seen in the experiment.

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