The electronic structure of the CoSi$_2$ (111) surface

L Magaud-Martinage, A Pasturel and F Cyrot-Lackmann

Laboratoire d'Etude des Propriétés Electroniques des Solides, Centre National de la Recherche Scientifique associé à l'Université Joseph Fourier, BP 166, 38042 Grenoble Cédex, France

Abstract. The electronic structure of the CoSi$_2$ (111) surface is studied within the tight binding approximation coupled with the decimation technique. The different geometries considered have either a Co- or a Si-bulk terminated surface and are called CoSi$_2$–Co and CoSi$_2$–Si respectively. The CoSi$_2$–Co surface shows a sharpening of the Co partial d density of states in relation with the reduction in the number of Co neighbours. In contrast, CoSi$_2$–Si presents a surface state with a Co-d character at 2.3 eV below the Fermi level. This result is compared with the surface state determined by Pirri *et al.*

1. Introduction

Many studies have already been made of the transition metal disilicides (TmSi$_2$) because of their technological interest. Most of these compounds are good metals and can be epitaxially grown on silicon to give Schottky barriers. For example, NiSi$_2$ and CoSi$_2$ have lattice mismatches of 0.4 and 1.2% with silicon (111) and form abrupt, perfect interfaces. So they have many potential applications in the Si device industry for producing transistors or superlattices. Their bulk electronic structure is now well known and it is governed by the Si-p–transition-metal-d hybridization (Speier *et al* 1989 and references therein). Much attention has been paid to the interface problem (Rees and Matthai 1988, Yongniam *et al* 1986, Bisi and Ossicini 1987, Ossicini *et al* 1990, Fujitani and Asano 1988, Das *et al* 1989a, b) but, to our knowledge, there have been hardly any theoretical studies of the electronic structure of the TmSi$_2$ surface (Rodrigues and Weisz 1989) and none in the case of CoSi$_2$. In addition to their fundamental interest, surface studies are very important as surfaces play an increasingly important role because of the decrease in device size. This has meant that their contribution is no longer negligible in comparison with that of the bulk. Furthermore, this surface is involved in the Si/CoSi$_2$ interface and knowledge of its electronic structure may give some insight into the interface problem.

We present here the first theoretical study of the electronic structure of the CoSi$_2$ (111) surface. The paper is organized as follows. The surface geometries we used and our calculation method are described in section 2 and the results are discussed in section 3.

2. Calculation procedure

CoSi$_2$ crystallizes in a cubic structure (fluorite). Many surface geometries have been proposed (Vrijmoeth *et al* 1989, Hellman and Tung 1988, Haderbache *et al* 1989) and we choose to study two of them. The first (named CoSi$_2$–Co) corresponds to bulk CoSi$_2$ cut on a cobalt plane while the second (CoSi$_2$–Si) has a complete CoSi$_2$ layer at the surface and hence ends on a silicon plane (figure 1). Adding a silicon plane to CoSi$_2$–Co gives a CoSi$_2$–Si surface.
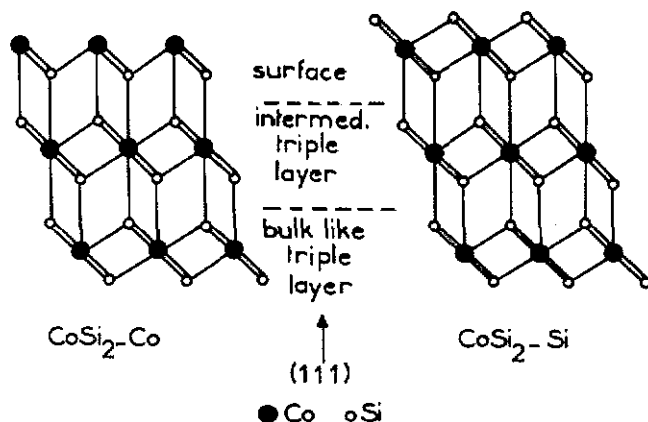

Figure 1. Co- and Si-terminated CoSi$_2$ (111) surfaces.

Calculations are performed within the tight binding approximation coupled to a decimation technique (Guinea *et al* 1983). The parameters have been fitted to the augmented plane wave (APW) band structure of bulk CoSi$_2$ as explained elsewhere (Martinage *et al* 1990). We use an orthogonal basis with s and p orbitals for silicon and d for cobalt since the APW calculation for bulk CoSi$_2$ has shown that Co s and p orbitals are not involved in Co–Si bonds. Furthermore, their densities of states (DOS) make a very small contribution to the total DOS, so we neglected them. Interactions between neighbours are introduced up to a distance $a/2$ where a is the lattice constant. This means that Co–Si and Si–Si interactions are taken into account. We assumed no surface relaxation occurred so we used the bulk parameters (table 1).

Table 1. CoSi$_2$ tight binding parameters (eV).

Si	Co	Si–Si	Si–Co
$E_s = -3.541$	$E_{t2g} = -2.054$	$ss\sigma = -1.431$	$sd\sigma = -1.023$
$E_p = 1.719$	$E_{eg} = -1.446$	$sp\sigma = 1.917$	$pd\sigma = -0.391$
		$pp\sigma = 2.336$	$pd\pi = 0.641$
		$pp\pi = -1.044$	

The so-called 'bulk-like' triple layer (figure 1) is connected to bulk CoSi$_2$ through some kind of self-energy matrix G_s which is a result of a decimation calculation on bulk CoSi$_2$.
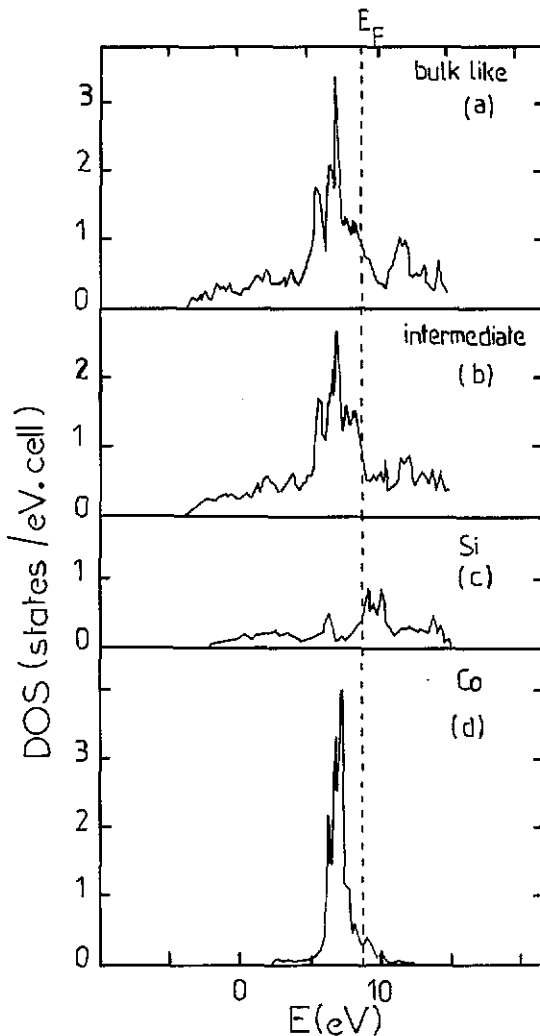
Figure 2. The DOS on the different planes of the CoSi₂–Co surface. (*a*) 'bulk-like' CoSi₂; (*b*) CoSi₂ intermediate triple layer; (*c*) the last Si plane; and (*d*) the Co surface plane.

Due to the surface, charge transfer occurs and creates an electrostatic potential which is treated in a self-consistent way on the five (CoSi₂–Co) or six (CoSi₂–Si) last atomic planes. Convergence is reached when the input and output potentials do not differ by more than 0.02 eV. The Hamiltonian is used to calculate the system's Green function $G = (E - H)^{-1}$ and then the DOS is given by

$$n(E) = -1/\pi \sum_{K \in ZBR} \operatorname{Im} G(k_{\parallel}, E)$$

The summation is performed with a special *k*-point technique (Cunningham 1974) with a set of nine *k*-points. We checked that this set was large enough by performing a calculation with 18 *k*-points. The difference between the two results was less than 0.02 eV for the main peaks positions.
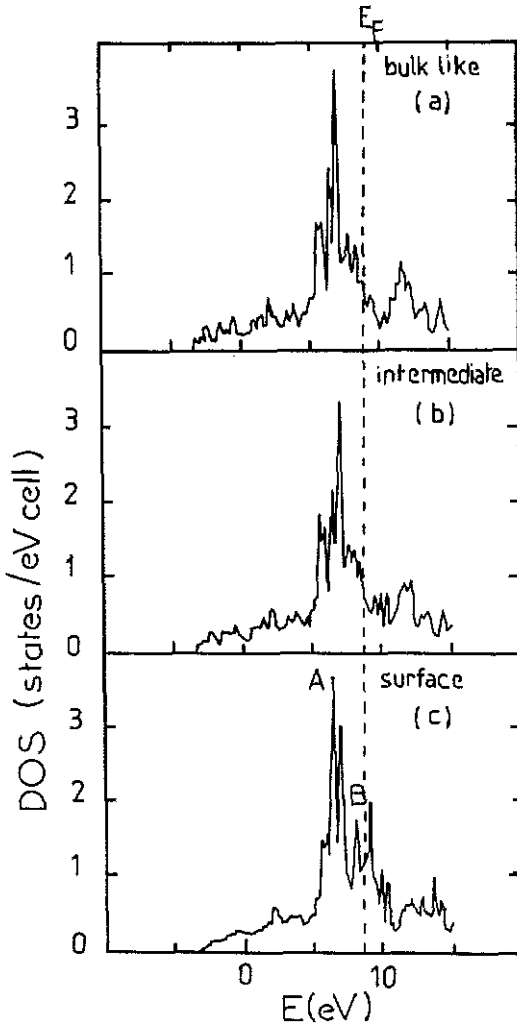
Figure 3. The DOS on the different planes of the CoSi$_2$–Si surface: (a) 'bulk-like' CoSi$_2$; (b) the intermediate triple layer; and (c) the surface triple layer.

3. Results and discussion

3.1. CoSi$_2$–Co surface

In figure 2, we show the DOSs on the different planes of the CoSi$_2$–Co surface. The 'bulk-like' CoSi$_2$ DOS (figure 2(a)) is in agreement with our previous bulk APW calculation (Martinage et al 1990). This clearly shows that we have introduced sufficient planes to treat the charge transfer. The bulk DOS exhibits Si-p–Co-d bonding and antibonding states on each side of the main peak due to Co non-bonding d-states. The Fermi level falls just before the pseudogap. This shape is maintained in the intermediate triple layer (figure 2(b)). DOSs for the last Si and Co layers are shown in figures 2(c) and 2(d). We notice a sharpening in the Co d-band in comparison with the bulk one. In fact, some bonding and antibonding Si-p–Co-d states have disappeared.

This is related to the reduction in the number of surface cobalt neighbours which goes from eight in the bulk to four in this case.

3.2. *CoSi₂–Si surface*

DOSs for the different planes of the $CoSi_2$–Si surface are shown in figure 3. As in $CoSi_2$–Co, the DOS on the 'bulk-like' and on the intermediate triple layers compare well with the $CoSi_2$ bulk DOS. The surface DOS is quite different. It exhibits two new peaks, the first one (A) falls just below the Co-d non-bonding states, at 2.3 eV below the Fermi level. The second one (B) is not so well defined and it is located at 0.6 eV below E_F. Both have the Co-d character. Peak A comes from the Co-d non-bonding peak splitting, and it corresponds to a surface state due to a peculiar Co–Co hybridization via surface silicon atoms.

This result can be compared with that of Pirri *et al* (1988). They studied the electronic structure of the $CoSi_2$ (111) surface using angle-resolved photoemission. The sample which has been determined (Haderbache *et al* 1989) to correspond to our $CoSi_2$–Si surface geometry exhibits two additional peaks. According to these authors, the first is a surface state with the Co-d character and falls 2.7 eV below the Fermi level. It corresponds to our A peak. Whether the second one located at 1.4 eV below E_F can be related to our B peak is not clear.

4. Conclusion

We have performed the first theoretical study of the electronic structure of the $CoSi_2$ (111) surface for two different geometries. In both cases, the surface only influences the first $CoSi_2$ triple layer. When the surface plane is made of Co atoms, the Co DOS is sharpened in relation with the decrease in the number of nearest neighbours to the surface atoms. For the Si-terminated surface, we find a surface state with the Co-d character in agreement with the experimental findings of Pirri *et al*.

References

Bisi O and Ossicini S 1987 *Surf. Sci.* **189/190** 285
Cunningham S L 1974 *Phys. Rev.* B **10** 4988
Das G P, Blöchl P, Christensen N E and Andersen O K 1989a *Metallization and Metal-Semiconductor interfaces (NATO Advanced Study Institute Ser. B, 195)* ed J P Batra (New York: Plenum) p 215
Das G P, Blöchl P, Christensen N E, Andersen O K and Gunnarson O 1989b *Phys. Rev. Lett.* **63** 1168
Fujitani F and Asano S 1988 *J. Phys. Soc. Japan* **57** 2253
Guinea F, Sanchez-Dehesa J and Flores F 1983 *J. Phys. C: Solid State Phys.* **16** 6499
Haderbache L, Wetzel P, Pirri C, Peruchetti J C, Bolmont D and Gewinner G 1989 *Appl. Surf. Sci.* **41/42** 257
Hellman F and Tung R T 1988 *Phys. Rev.* B **37** 10786
Martinage L, Pasturel A, Papaconstantopoulos D A and Cyrot-Lackmann F 1990 *Physica Scripta* **42** 363
Ossicini S, Bisi O and Bertoni C M 1990 *Phys. Rev.* B **42** 5735
Pirri C, Gewinner G, Peruchetti J C, Bolmont D and Derrien J 1988 *Phys. Rev.* B **38** 1512
Rees N V and Matthai C C 1988 *J. Phys. C: Solid State Phys.* **21** L981
Rodrigues D E and Weisz F J 1989 *Phys. Rev.* B **39** 1622
Speier W, van Leuken E, Fuggle J C, Sarma D D, Kumar L, Dauth B and Buschow K H J 1989 *Phys. Rev.* B **39** 6008
Vrijmoeth J, Schins A G and van der Veen J F 1989 *Phys. Rev.* B **40** 3121
Yongniam X, Kaiming Z and Xide X 1986 *Phys. Rev.* B **33** 8602