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The effect of silicon vacancies on the electronic structure of yttrium disilicide

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Abstract. *Ab initio* calculations of the electronic structure of yttrium disilicide have been performed using the LMTO–ASA method (linear muffin-tin orbitals in the atomic sphere approximation). Two different cases have been investigated: stoichiometric YSi_2 and silicon-deficient $YSi_{1.7}$ where one silicon atom out of every six is missing. We show that the main effect of these vacancies is to shift the Fermi level towards a region of much lower density, thus stabilizing the structure.

1. Introduction

Rare-earth disilicides ($RESi_2$) are of great interest for technological applications in infra-red detectors, for example. Many of them (RE = Gd to Lu) can be epitaxially grown on Si 111 with a very small lattice mismatch (Knapp and Picraux 1986), and the resulting interface is of high crystalline quality (d'Anterroches Meneau 1990), similar to the best transition-metal-disilicide–silicon ones ($CoSi_2$/Si–$NiSi_2$/Si, Derrien and Arnaud d'Avitaya 1987, Ospelt *et al* 1988). What makes them so interesting is that these interfaces have unusually low Schottky barriers (Tu *et al* 1981, Duboz *et al* 1989): Φ_n=0.35 eV on n-doped silicon compared with 0.65 to 0.75 eV for all the other known silicide–silicon interfaces (Nicolet and Lau 1983). No explanation has been found up to now for such a low value.

These compounds have another peculiarity: they crystallize in a hexagonal lattice with silicon vacancies (Baptist *et al* 1988, 1990). One silicon atom out of every six is missing, resulting in an $RESi_{1.7}$ stoichiometry. A periodic rearrangement of these vacancies is the most probable hypothesis, although this has not been definitely established. In fact, only surface reconstruction has been demonstrated, but it has been proposed that there is reconstruction in the bulk also (Knapp and Picraux 1986, Baptist *et al* 1990). The effect of the vacancies in the Schottky barrier at the interface with silicon is not known but, before going on to study the interface, one needs to know what their influence is on the bulk electronic structure. This paper presents electronic structure calculations for two different cases: YSi_2 and Si-deficient $YSi_{1.7}$. we chose to study yttrium disilicide because Y has no f electrons and this simplifies the calculation. Y is not properly speaking a rare earth, but is generally associated with these elements because of its properties. YSi_2 has the same crystallographic structure, the same electronic structure (if we except the f electrons) and the same

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low Schottky barrier on silicon as the other rare-earth disilicides. Furthermore, experiments have shown that the 4f states are not important as far as the electronic structure is concerned, but that they are atomic-like ($ErSi_2$, Veuillen *et al* 1991b; $TbSi_2$, Veuillen *et al* 1991a). YSi_2 is representative of all the $RESi_2$ that can be epitaxially grown on silicon, with RE going from Gd to Lu. In a previous calculation for stoichiometric YSi_2 by the APW method (Magaud *et al* 1992) we suggested that the effect of the Si vacancies is to shift the Fermi level to lower energies corresponding to a smaller density of states at E_F. This prediction is now quantitatively confirmed by the present supercell LMTO calculation.

2. Computational details

YSi_2 crystallizes in a hexagonal structure of the AlB_2 type with three atoms per unit cell. Along the c axis, the AlB_2 structure is made up of alternating Si ($z = c/2, 3c/2, \ldots$) and Y ($z = 0, c, \ldots$) planes and the lattice constants are $a = 3.842$ Å and $c = 4.14$ Å. The projection of the AlB_2 unit cell along the c axis is shown in the shaded zone of figure 1. There is experimental evidence for the presence of silicon vacancies in this structure; one silicon atom out of every six is missing, resulting in a $YSi_{1.7}$ stoichiometry. Experiments have shown the existence of a $\sqrt{3} \times \sqrt{3}$ R30 surface reconstruction (reconstruction $\sqrt{3} \times \sqrt{3}$ with a rotation of 30° of the a and b axis along the c axis). This reconstruction has been proposed for the bulk too and we used it in the calculation. The corresponding unit cell is shown in figure 1(*a*). It is three times bigger than that of YSi_2 and contains eight atoms: three of Y and five of Si. Two types of silicon atom appear: Si1 which has the same first neighbours as it does in YSi_2, and Si2 which has one vacancy in its first neighbours. This structure is equivalent to that of Yb_3Si_5 (Iandelli *et al* 1979). The vacancies induce atomic relaxation as shown in figure 1. Because of the symmetry, only the Y and Si2 atoms move. We used the experimental atomic positions determined by Iandelli *et al* (1979) for bulk Yb_3Si_5. They are given in table 1.

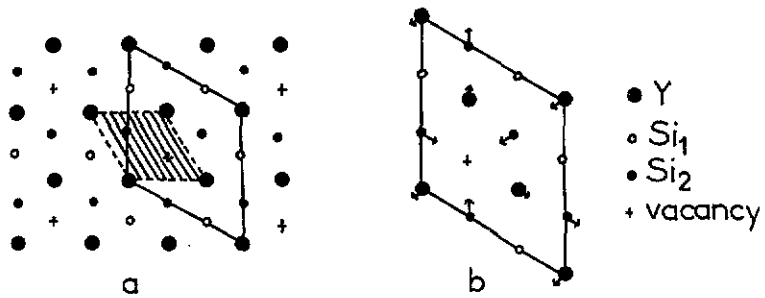

Figure 1. Crystallographic structure. (*a*) YSi_2 and non-relaxed $YSi_{1.7}$. In YSi_2, all Si1, Si2 and vacancy sites are equivalent and occupied by a silicon atom. (*b*) Relaxed $YSi_{1.7}$ (Yb_3Si_5); the arrows point to the relaxed atomic positions. The YSi_2 unit cell is shown shaded and that of $YSi_{1.7}$ is unshaded.

The calculations are carried out using a scalar-relativistic LMTO–ASA code (Andersen 1975). It uses the density functional formalism (Hohenberg and Kohn 1964, Kohn and Sham 1965). The local density approximation (LDA) is used for the exchange and correlation potentials, and they are expressed according to the von Barth and

Table 1. Atomic positions in YSi_2 and relaxed $YSi_{1.7}$ (Iandelli *et al* 1979). The number of atoms in the $\sqrt{3} \times \sqrt{3}$ R30 unit cell are indicated in parentheses.

	YSi_2	Relaxed $YSi_{1.7}$
Y (3)	x' 0 0	x' 0 0
	$x' = 0.333$	$x' = 0.358$
Si1 (2)	$\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$	$\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$
Si2 (3)	x 0 $\frac{1}{2}$	x 0 $\frac{1}{2}$
	$x = 0.666$	$x = 0.745$
Vacancy (1)	$\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$	$\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$

Hedin formulation (von Barth and Hedin 1972). The basis functions include angular momenta up to $l = 2$ for yttrium and silicon.

The k-integrations are performed using the tetrahedron method (Jepsen and Andersen 1971). Convergence is first searched for on a grid of 50 (180) k-points in the reduced Brillouin zone—that is, 512 (512) over the whole zone for YSi_2 ($YSi_{1.7}$). We then go on with 216 (546) k-points in the reduced zone—that is, 3375 (1728) over the whole zone. We have checked that the results for the two different sets are very similar in the two cases (YSi_2 and $YSi_{1.7}$) to be sure that the sets we use are large enough to give a good convergence. The sphere radii are the following for YSi_2: $R_Y = 1.991$ Å and $R_{Si} = 1.337$ Å. There was no need to introduce an empty sphere because of the compacity of the AlB_2 structure, in agreement with the previous work of Fujitani and Asano (1990). For relaxed $YSi_{1.7}$, we made several investigations with different sphere radii for Y, Si1, Si2 and the empty sphere on the vacancy site to find a good compromise between the sphere overlaps, which must be smaller than 30–35%, and the charge transfer between the spheres. We found that if we introduce an empty sphere to simulate the vacancy, its radius must be at least three times smaller than the others. Although the meaning of an LMTO calculation under such conditions is questionable, we still performed it and we did not find noticeable modifications of the DOS compared with the ones presented here. The results shown here have been obtained with no empty sphere on the vacancy site. The sphere radii have been adjusted to fill all of the space. This is possible because in this structure the atomic displacements are rather important and 'hide' the vacancy. The sphere radii are $R_Y = 1.863$ Å, $R_{Si1} = 1.563$ Å and $R_{Si2} = 1.534$ Å and the overlaps do not exceed 38%.

3. Results

YSi_2 densities of states (DOS) are shown in figure 2. Under the Fermi level, the DOS can be divided into three parts. The first one extends from the bottom of the band up to −0.6 Ryd and has an Si s character. The second one, from −0.6 to −0.45 Ryd, is mainly of silicon p character. The third one extends up to the Fermi level. The Y d contribution increases on approaching E_F. The DOS in figure 2 is in good agreement with that obtained in our previous calculation using the APW method (Magaud *et al* 1992) and the Fujitani result obtained using the LMTO method (Fujitani and Asano 1990). The Fermi level falls in a strong density peak indicating that the structure is not stable. A shift of the Fermi level towards lower energies, in the nearby density trough, would stabilize it. In a rigid-band-scheme approach, this kind of shift can

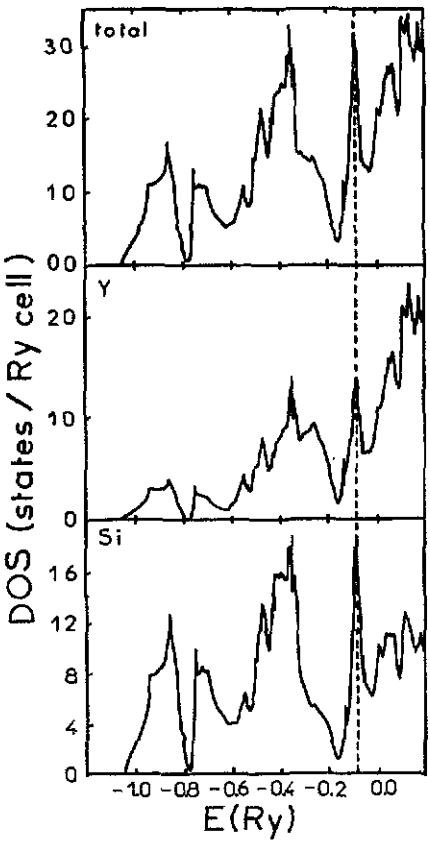

Figure 2. Total and partial DOS of YSi_2 in the AlB_2 structure. Note the different scales for the DOS.

originate from the vacancies. This is confirmed in the following, with the $YSi_{1.7}$ calculation.

The effect of the vacancies on the densities of states is shown in figure 3. The general shape of the DOS remains identical and the region below the Fermi level can still be divided into three parts. The contributions of the different states to the structures remain the same. The same increase of the Y d-state contribution to the DOS is found on approaching the Fermi level, in agreement with experiment (Braïcovitch *et al* 1990). The effect of the vacancies is to shift the Fermi level towards lower energies, as one would expect from a rigid-band-shift argument. The distance between the main peak and the Fermi level decreases by 1.5 eV in the total DOS. This confirms a previous finding (Magaud *et al* 1992) that a shift of -1.3 eV of the Fermi level would improve the agreement between the YSi_2 theoretical DOS and XPS spectra. The main peak falls at the same position in the Si1 and Y partial DOS. This position is close to that observed in YSi_2 (with E_F shifted by -1.5 eV). It is 0.35 eV lower in the Si2 partial DOS. The difference between the two silicon DOS arises from the Si2 environment being more disturbed by the vacancies.

In $YSi_{1.7}$ DOS, the Fermi level falls in a low-density region. The DOS at E_F is nearly two times smaller in $YSi_{1.7}$ than in YSi_2, which is a good indication of the stability of this lacunary structure compared with that of the AlB_2 one.

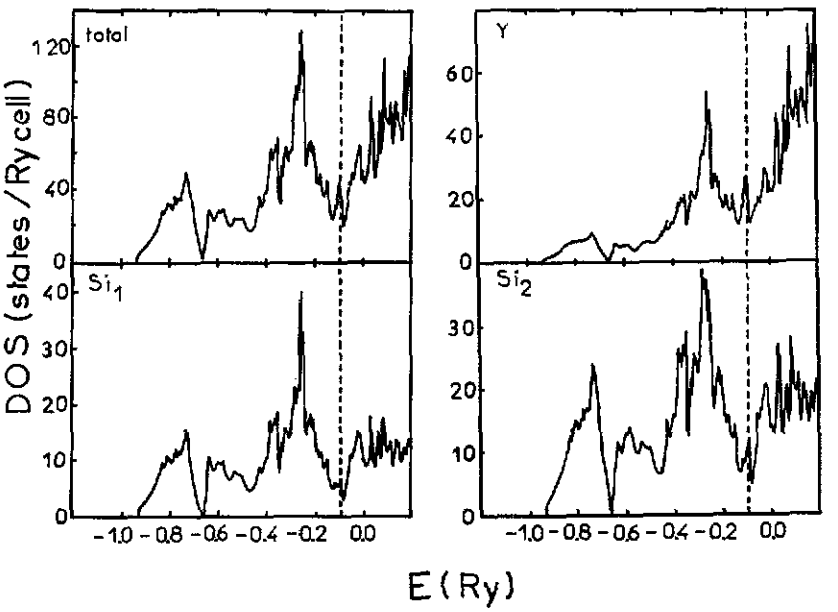

Figure 3. Total and partial DOS of $YSi_{1.7}$ in the Yb_3Si_5 structure. Note the different scales for the DOS.

4. Conclusion

We have performed the first *ab initio* study of the electronic structure of $YSi_{1.7}$, assuming a periodic arrangement of the Si vacancies. The calculations have shown that the main effect of the vacancies is to shift the Fermi level towards lower energies as suggested in a previous study. In $YSi_{1.7}$, the Fermi level falls in a low DOS region, indicating that the lacunary structure (Yb_3Si_5) is more stable than the stoichiometric AlB_2 structure.

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