Structural effects on the calculated semiconductor gap of CrSi2

L. F. Mattheiss

AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 16 October 1990)

The results of band calculations for hexagonal CrSi2, carried out in the local-density approximation, predict an indirect semiconductor gap of 0.30 eV which is in excellent agreement with the measured optical value ($\sim$0.35 eV). The calculated gap, which occurs within the Cr $3d$ manifold, is particularly sensitive to the local Cr-Si coordination geometry. It decreases with uniaxial pressure along c and vanishes for the alternative sequencing of hexagonal-type CrSi2 layers that characterize the orthorhombic and tetragonal phases of the refractory (groups IV-VI) transition-metal disilicides.

Transition-metal silicides have received increased attention in recent years because of their practical importance in silicon-based microelectronics as Schottky barriers and low-resistivity interconnects.[1,2] The refractory disilicides RSi2 (i.e., those containing groups IV-VI transition-metal elements R) are especially attractive in such applications because of their high-temperature stability and generally low electrical resistivities. Unlike their cubic group-VIII counterparts CoSi2 and NiSi2, the refractory disilicides RSi2 form with a variety of complicated, low-symmetry orthorhombic, hexagonal, and tetragonal structures. Despite their apparent diversity, these phases share a common structural element, namely, nearly hexagonal RSi2 layers.[3] These compounds also share similar electronic properties[4] (i.e., partially filled d bands near E_F), which presumably account for their novel structural and thermal properties.

Although most transition-metal silicides are metallic, a few compounds have been characterized as semiconductors, with typical band gaps in the (0.1-0.9)-eV range.[2] Among these semiconductors, the refractory compound CrSi2 has been the most extensively studied material since its initial characterization as an 0.35-eV band-gap semiconductor in the mid-1960s.[5] The analysis of subsequent transport data[6] has yielded a slightly smaller estimate ($\sim$0.30 eV) of the CrSi2 band gap, along with indications of relatively large hole and electron effective-mass ratios ($m^*/m_0\sim$3 and 20, respectively). Such masses seem consistent with the enhanced Cr $3d$ character near E_F that is expected for a refractory compound.

Potential optoelectronic device applications that combine semiconductor-semiconductor heterojunctions with silicon-based integrated-circuit technology have stimulated efforts to grow epitaxial CrSi2 thin films on various faces of Si.[7,8] Despite a favorable lattice match with Si(111), these attempts have produced small grained ($\sim$2 μm) epitaxial regions that cover only a fraction ($\sim$70%) of the total interface. A promising technique for fabricating Si/CrSi2/Si heterostructures with improved interfaces utilizes ion implantation to form thin buried layers of CrSi2 in Si(111) wafers.[9]

At present, a detailed understanding of the nature and origin of the semiconducting gap in CrSi2 is lacking. One proposal[1] suggests that magnetic influences may be important. Indeed, the results of a band calculation[10] for hexagonal CrSi2 predict semimetallic rather than semiconducting behavior. However, recent optical studies[11] have provided convincing evidence that a standard band-like picture is applicable. According to these measurements, CrSi2 has an indirect band gap of $\sim$0.35 eV, with indications of strong direct transitions at slightly higher ($\sim$0.67 eV) energies.

These developments have stimulated the present effort to explore the applicability of a simple band picture for explaining the semiconductor gap in hexagonal CrSi2. With this objective, the linear augmented-plane-wave (LAPW) method has been applied to calculate the electronic band structure of bulk hexagonal CrSi2 in the local-density approximation (LDA). The present implementation of the LAPW method[12] imposes no shape approximations on either the crystalline charge density or the potential. Exchange and correlation effects are treated with the use of the Wigner interpolation formula.[13] The present calculations include a basis of $\sim$500 LAPW's (12 Ry plane-wave cutoff) and spherical-harmonic terms through $l=6$. The crystalline charge density and potential are expanded with about 5000 plane waves (55 Ry) in the interstitial region and lattice harmonics ($l_{max}=4$) within the muffin-tin spheres. A 14-point $\mathbf{k}$ mesh in the irreducible $\frac{1}{24}$ wedge has been used to carry out Brillouin-zone integrations.

The essential features of the hexagonal $C40$ structure are illustrated in Fig. 1. It consists of identical hexagonal CrSi2 layers which are stacked in an ABC sequence such that successive layers are rotated by 60° about an origin ($*$). The intralayer Cr-Si bond lengths ($\sim$2.55 Å) are determined by a Si-atom position parameter x. Total-energy calculations[14] show that deviations from the "ideal" $x=\frac{1}{6}$ value[15] are minimal ($\Delta x=1.5\times10^{-4}$). The $C40$ space group (D_6^4) is nonsymmorphic, containing a screw axis that interchanges layers via the nonprimitive translations $\tau=0$, $c/3$, and $2c/3$. $E_{n,\mathbf{k}}$ exhibits full hexagonal (D_{6h}) symmetry as a result of time reversal.[16] The orthorhombic and tetragonal phases that characterize the other refractory disilicides (see Table I) involve alternative four-layer ($ABCD$ for $C54$) or two-layer (AB' for $C49$ and AB for $C11_b$) variations on the three-layer ABC stacking of the hexagonal $C40$ phase.[3] The ubiquity of these hexagonal RSi2 layers implies an intrinsic stability that should enhance their epitaxial growth at Si inter-
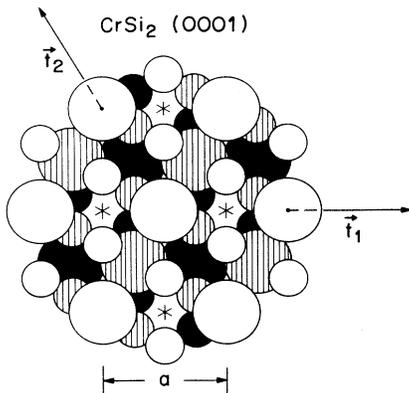
FIG. 1. Projected (0001) view of hexagonal $C40$ CrSi$_2$ illustrating the ABC stacking of hexagonal CrSi$_2$ layers. Cr (Si) atoms are represented by the large (small) circles; neighboring primitive-cell origins are labeled with *'s.

FIG. 2. LAPW energy-band results for hexagonal ($C40$) CrSi$_2$. Triangles identify bands with significant Si $3s,3p$ orbital weight ($> 15\%$) within the Si muffin-tin spheres.

faces.

Because the $C40$ structure contains three formula units per primitive cell, a complex band structure can be anticipated for hexagonal CrSi$_2$. These expectations are realized in the LAPW band results which are shown in Fig. 2. As indicated by the triangle symbols, the lowest CrSi$_2$ bands have predominant Si $3s,3p$ character, which then gradually switches to Cr $3d$ character near E_F. Within this Cr $3d$ manifold, an 0.30-eV indirect band gap occurs between the highest filled valence-band state $E_{n,\mathbf{k}}$ at L ($n = 21$) and the lowest unoccupied conduction-band state at M ($n = 22$). This calculated LDA gap is in excellent agreement with the measured 0.35-eV optical gap.[11] However, the calculated lowest-energy direct transition at L is somewhat smaller than the observed value (0.45 vs 0.67 eV).

The origin of the CrSi$_2$ band gap within the Cr $3d$ manifold is rather complex, involving the hybridization of specific $3d$ orbitals with the Si $3p$ states in neighboring layers. As shown in the upper portion of Fig. 3, states near the valence-band maximum have predominant $d_{3z^2-r^2}$ symmetry while the conduction-band minimum involves $d_{xz,yz}$-type states. Despite substantial d character, the calculated effective masses are close to the free-electron values for both the valence and conduction bands. Specifically, the principal-axis effective-mass ratios for

TABLE I. Observed crystal structures of the refractory transition-metal disilicides RSi_2 (Ref. 2). O, H, and T denote phases with orthorhombic, hexagonal, and tetragonal symmetry, respectively.

| | | Group | |
Series	IV	V	VI
$3d$	TiSi$_2$	VSi$_2$	CrSi$_2$
	$O(C54)$	$H(C40)$	$H(C40)$
$4d$	ZrSi$_2$	NbSi$_2$	MoSi$_2$
	$O(C49)$	$H(C40)$	$T(C11_b)$
$5d$	HfSi$_2$	TaSi$_2$	WSi$_2$
	$O(C49)$	$H(C40)$	$T(C11_b)$

holes [electrons] at L [M] are (1.2, 1.3, 0.9) [0.7, 0.7, 1.4]. These are significantly smaller than the corresponding experimental values of $\sim 3[20]$.[6] Clearly, independent measurements would be useful in clarifying this discrepancy.

The excellent agreement between the calculated CrSi$_2$ band gap and experiment is unanticipated, since the LDA greatly underestimates semiconductor band gaps in many other systems. Its success in CrSi$_2$ may be understood in terms of the analysis of the many-body self-energy operator given by Godby, Schlüter, and Sham.[17] They showed that the spatial nonlocality of this operator was the dominant characteristic which produced accurate band gaps. When integrated against the relatively smooth valence-band wave functions, it produced a more attractive effective potential than the more rapidly oscillating conduction-band functions.[17] While such qualitative differences between the valence- and conduction-band states are found in the conventional group IV and III-V semiconductors, the dominant spatial scale of nearby states on both sides of the CrSi$_2$ band gap is the same, set by the Cr $3d$ orbitals. As noted above, the CrSi$_2$ gap originates from a subtle combination of hybridization and crystal-field effects which do not modify significantly the shape of the high-amplitude $3d$ portion of these wave functions. It is, therefore, plausible that the state dependence of the self-energy should be small within this group of bands, and the band splittings accurately represented by the LDA potential.[18]

Because of its small value, one can expect the calculat-

CrSi$_2$ (C40)

CrSi$_2$ (C11$_b$)

CrSi$_2$ (C54)
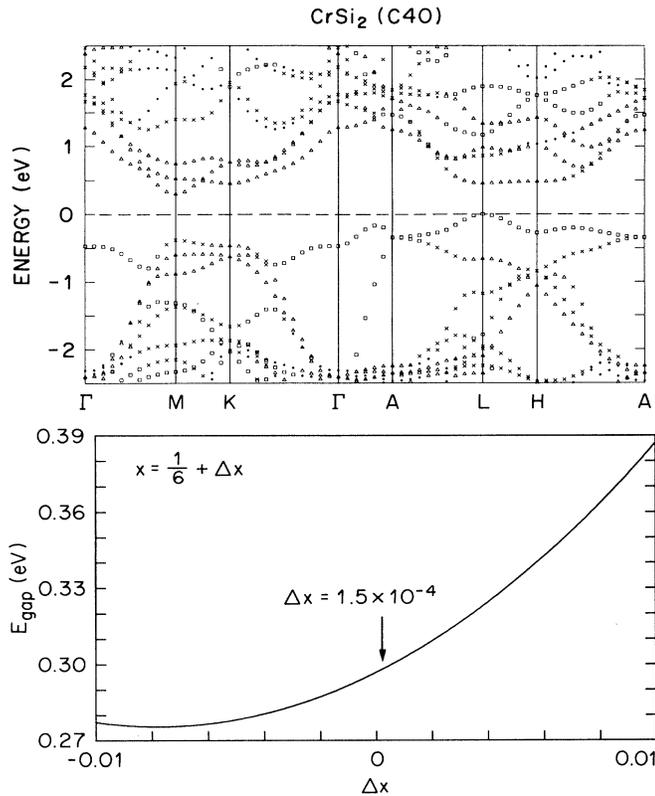
FIG. 3. LAPW energy-band results near E_F for hexagonal CrSi$_2$. Bands with specific $3d$-orbital character are distinguished by squares $(d_{3z^2-r^2} > 15\%)$, triangles $(d_{xz,yz} > 30\%)$, and x's $(d_{xy,x^2-y^2} > 30\%)$. Calculated dependence of the CrSi$_2$ band gap E_{gap} on the Si-atom position parameter x.

FIG. 4. Effect of alternative layer sequencing on the CrSi$_2$ bands near E_F, including the AB and $ABCD$ stacking of the tetragonal $(C11_b)$ and orthorhombic $(C54)$ phases. The squares identify bands with dominant Cr $3d$ orbital character $(d > 50\%)$.

ed CrSi$_2$ band gap to be sensitive to both structural and chemical changes. Substantially reduced gaps are calculated[14] for the metastable $C40$ phases of MoSi$_2$ (+0.02 eV) and WSi$_2$ (−0.03 eV). Analogous calculations show that a 2% reduction in the CrSi$_2$ c-axis lattice parameter causes an 8-meV decrease in the band gap. The calculated gap is particularly sensitive to the Si-atom position parameter x that determines the Cr-Si coordination geometry within each CrSi$_2$ layer. In the results presented thus far, this parameter has been fixed at its ideal $x = \frac{1}{6}$ value, where each Si atom has six equidistant planar neighbors. The dependence of the CrSi$_2$ band gap E_{gap} on small Δx variations is shown in the lower portion of Fig. 3. It is seen that E_{gap} varies by ~0.1 eV for Δx changes of ±0.01. However, the resulting increase in the predicted CrSi$_2$ band gap is minimal (~1 meV) for the calculated shift,[14] $\Delta x \approx 1.5 \times 10^{-4}$.

The effect of stacking sequence changes on the CrSi$_2$ bands near E_F is illustrated in Fig. 4. In these calculations, lattice parameters for the tetragonal $C11_b$ and orthorhombic $C54$ phases have been derived from the $C40$ values[15] $(a = 4.420$ Å, $c = 6.349$ Å) using the relations $a_t = \sqrt{2}a/2$, $c_t = \sqrt{3}a$, and $a_0 = \sqrt{3}a$, $b_0 = a$, $c_0 = 4c/3$. These parameters preserve the $C40$ intraplanar CrSi$_2$ bond distances in both phases. Tetragonal symmetry increases the $C40$ CrSi$_2$ interlayer separation from 2.12 to

2.21 Å for the $C11_b$ phase. However, the $C40$ geometry is changed only in the fourth layer (~8.5 Å) in the $C54$ calculation.

As shown by the results in Fig. 4, both hypothetical forms of CrSi$_2$ exhibit semimetallic behavior. The tetragonal $(C11_b)$ results are in good agreement with those[19] for the isostructural compounds MoSi$_2$ and WSi$_2$. In the $C54$-phase results, the slight (~0.05 eV) band overlap is the result of increased hybridization of the Cr $3d$ states with Si $3p$ orbitals. Thus, a subtle combination of symmetry and distant-neighbor (~8.5 Å) coordination changes is sufficient to eliminate the $C40$ CrSi$_2$ band gap. The calculations show that the total energies of all three CrSi$_2$ phases are comparable, with the $C11_b$ (~0.01 eV/formula unit) and $C54$ (~0.1 eV/formula unit) phases slightly less stable than $C40$ CrSi$_2$. This suggests the possible presence of low-energy stacking faults in thin-film CrSi$_2$ samples, a potential detriment in device applications that exploit the semiconducting properties of bulk CrSi$_2$.

To summarize, band calculations confirm that hexagonal CrSi$_2$ is a small-gap semiconductor, yielding a band gap of 0.30 eV which is in excellent agreement with experiment. This calculated gap is sensitive to subtle structural-symmetry variations that transform the $C40$ phase into the closely related $C54$ and $C11_b$ structures.

L. F. MATTHEISS

[1]S. P. Murarka, J. Vac. Sci. Technol. **17**, 775 (1980).

[2]M.-A. Nicolet and S. S. Lau, in *VLSI Electronics:* Microstructure Science, Vol. 6, edited by N. G. Einspruch and G. B. Larrabee (Academic, New York, 1983), p. 329.

[3]F. Laves, in *Theory of Alloy Phases* (American Society for Metals, Metal Park, Cleveland, OH, 1956), p. 181.

[4]J. H. Weaver, A. Franciosi, and V. L. Moruzzi, Phys. Rev. B **29**, 3293 (1984).

[5]D. Shinoda, S. Asanabe, and Y. Sasaki, J. Phys. Soc. Jpn. **19**, 269 (1964).

[6]I. Nishida and T. Sakata, J. Phys. Chem. Solids **39**, 499 (1978).

[7]F. Y. Shiau, H. C. Cheng, and L. J. Chen, Appl. Phys. Lett. **45**, 524 (1984); J. Appl. Phys. **59**, 2784 (1986).

[8]R. W. Fathauer, P. J. Grunthaner, T. L. Lin, K. T. Chang, J. H. Mazur, and D. N. Jamieson, J. Vac. Sci. Technol. B **6**, 708 (1988).

[9]A. E. White, K. T. Short, and D. J. Eaglesham, Appl. Phys. Lett. **56**, 1260 (1990).

[10]A. Franciosi, J. H. Weaver, D. G. O'Neill, F. A. Schmidt, O. Bisi, and C. Calandra, Phys. Rev. B **28**, 7000 (1983).

[11]M. C. Bost and J. E. Mahan, J. Appl. Phys. **63**, 839 (1988).

[12]L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **33**, 823 (1986).

[13]E. Wigner, Phys. Rev. **46**, 1002 (1934).

[14]Details will be provided in a separate publication.

[15]W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, New York, 1958).

[16]M. Lax, *Symmetry Principles in Solid State and Molecular Physics* (Wiley, New York, 1974).

[17]R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986); Phys. Rev. B **36**, 6497 (1987).

[18]R. O. Jones and O. Gunnarsson, Phys. Rev. Lett. **55**, 107 (1985).

[19]B. K. Bhattacharyya, D. M. Bylander, and L. Kleinman, Phys. Rev. B **32**, 7973 (1985).