# Electronic structure and optical properties of $\beta$-$FeSi_2$

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We have investigated the optical properties of $\beta$-$FeSi_2$ experimentally and theoretically. The measured optical functions were compared with those calculated using the local-density-functional theory and the linear muffin-tin orbital method. The calculated electronic structure is analyzed using orbital-projected densities of states and the optical functions are interpreted in terms of interband transitions. We find generally excellent agreement between theory and experiment. [S0163-1829(98)00116-7]

## I. INTRODUCTION

The current interest in transition-metal silicides (TMS) is due to their high-temperature stability, resistance to degradation, and high electrical conductivity, which make them suited as Schottky barriers, Ohmic contacts, and interface diffusion barriers in microelectronic devices.[1] In the past few years, extensive work on the electronic structure and physical properties of TMS has been performed.[2–7] The attention in this field has been concentrated on the epitaxial growth of high-quality samples of some specific compounds considered particularly interesting and promising in their applications.[8] While most of the silicides studied so far are metallic and thus interesting for the production of connections and high-quality Schottky barriers to Si, $\beta$-$FeSi_2$ is a semiconductor.

$FeSi_2$ exists in two thermodynamically stable phases: a tetragonal, metallic $\alpha$-$FeSi_2$ phase and an orthorhombic semiconducting $\beta$-$FeSi_2$ phase.[9] The phase-transition temperature is 937 °C,[10] where $\beta$-$FeSi_2$ is the low-temperature stable phase. $\beta$-$FeSi_2$ has an indirect band gap of about 0.78 eV and a slightly larger direct gap of about 0.83–0.89 eV,[11–14] matching the transmission window of $SiO_2$ optical fibers at 1.55 $\mu$m quite well. This feature, added to the possibility of growing $\beta$-$FeSi_2$ films epitaxially on both (111) and (100) Si substrates,[15] opens interesting perspectives for application in optoelectronic devices based on silicon technology.

The band-structure calculation of $\beta$-$FeSi_2$ has been done by Christensen[16] using the linear muffin-tin orbital (LMTO) atomic sphere approximation (ASA) method. The formation of the band gap in $\beta$-$FeSi_2$ was described in terms of a Jahn-Teller-like transition from a metallic $FeSi_2$ phase in a hypothetical $CaF_2$ structure to the orthorhombic $\beta$ phase. The gap was found to be equal to 0.8 eV, in good agreement with experimental data. The LMTO calculations in this work were performed strictly within the ASA and did not include the so-called combined-correction term, which reduces the gap in semiconductors.[17] In the electronic-structure calculations of Eppenga[18] using the augmented-spherical-wave method and including the combined-correction term, an indirect gap of 0.44 eV was obtained. The energy-band structure and soft-x-ray-emission and -absorption spectra of $\beta$-$FeSi_2$ were calculated by the full-potential linearized augmented plane-wave method by Eisebitt *et al.*[19] An indirect band gap of 0.78 eV and a direct band gap of 0.82 eV were determined. Band-structure calculations by the linear muffin-tin orbital method in the local-density approximation (LDA) including exchange and correlation by Filonov *et al.*[20] yielded an indirect gap between 0.738 and 0.75 eV and a direct gap of 0.825 eV.

In this paper we present the optical spectra of $\beta$-$FeSi_2$ [the reflectivity $R(\hbar\omega)$, the conductivity $\sigma(\hbar\omega)$, the real $\varepsilon_1(\hbar\omega)$, and the imaginary $\varepsilon_2(\hbar\omega)$ part of the dielectric function], obtained by reflectance and ellipsometric measurements. We compare these with first principles local-density-functional[21] (LDA) calculations using the LMTO method in the ASA.[22,23] We find good detailed agreement between all these experiments and the calculated spectra, which leads us to the conclusion that the LDA gives a consistent picture of the electronic structure in $\beta$-$FeSi_2$.

## II. EXPERIMENT

The $\beta$-$FeSi_2$ layers studied were grown in a ultrahigh vacuum molecular-beam epitaxy (MBE) growth chamber on Si(100) substrates using the template technique.[24] The template layer formation was carried out by two deposition steps. In a first step Fe and Si were coevaporated with a small Fe excess onto the unheated substrate and subsequently annealed at 420 °C. The thickness of this first layer was around 0.9 nm. Reflection high-energy electron-diffraction observations now show the known $\beta$-$FeSi_2$ pattern for the epitaxial relationship $\beta$-$FeSi_2$(100)/Si(100) with mostly type-*A* orientation.[25] After cooling down Fe and Si were then coevaporated in stochiometric proportion onto the unheated substrate and annealed at 660 °C to increase the template layer thickness. The total layer thickness was now around 4.7 nm. During further epitaxial growth to the desired film thickness of approximately 200 nm the substrate temperature was kept close to 660 °C.

Optical reflection spectra from 0.5 to 6.2 eV were measured with a Perkin-Elmer UV-VIS-NIR Lambda 19 spec-

 

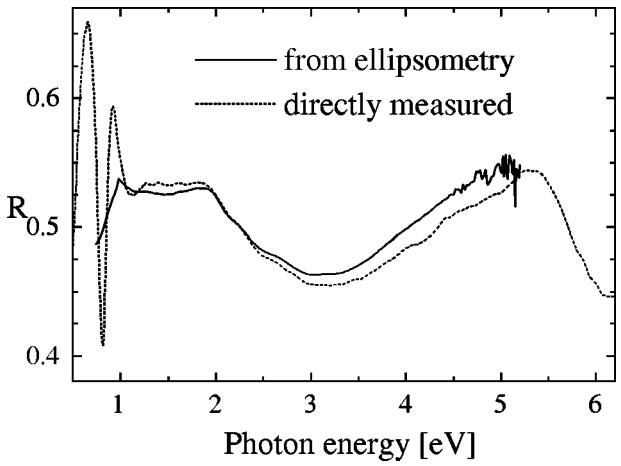


FIG. 1. Directly measured reflectance (dashed line) in comparison with the reflectivity calculated from the ellipsometrically measured optical constants (solid line) for $\beta$-$FeSi_2$ epitaxial film.

trometer. The specularly and diffusively reflected light was recorded by an integrating sphere. Spectroscopic ellipsometry measurements were carried out on a Woollam VASE ellipsometer over the energy range 0.75–5.1 eV.

In a first run ellipsometric measurements were done immediately after having removed the sample from the MBE apparatus in order to minimize oxide layer formation on the surface, using a rough mesh of measuring points. In later measurements a decrease in the magnitude of the pseudo-optical constants was preferentially noticed in $\langle \varepsilon_2 \rangle$ above 3 eV due to oxide layer formation. The final values for the optical constants of the $\beta$-$FeSi_2$ film were then obtained with a closer spacing of points by removing the grown $SiO_2$ layer numerically using a three-layer model (Si-substrate $|\beta$-$FeSi_2|SiO_2$).

In order to verify the consistency of optical data recording, Fig. 1 shows a comparison of the directly measured reflectance with the reflectivity calculated on the basis of the ellipsometrically determined optical constants. As may be seen, there is good agreement between 1 and 5 eV. Towards lower energies interference patterns appear in the directly measured reflectance due to light passage through the layer because of decreasing absorption and its reflection from the back surface.

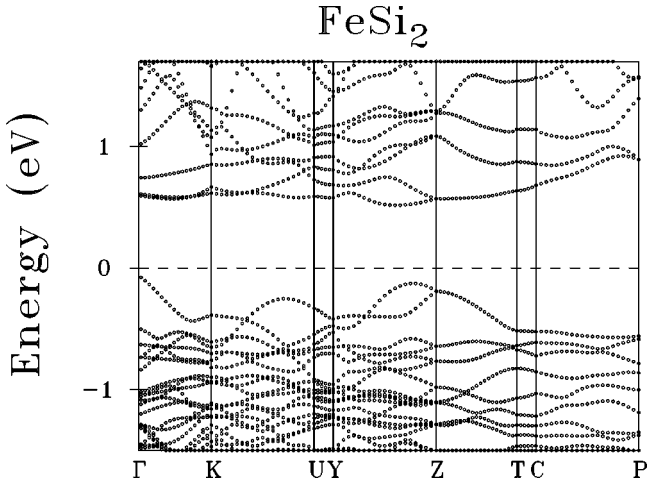


FIG. 2. Self-consistent energy-band structure of $\beta$-$FeSi_2$.

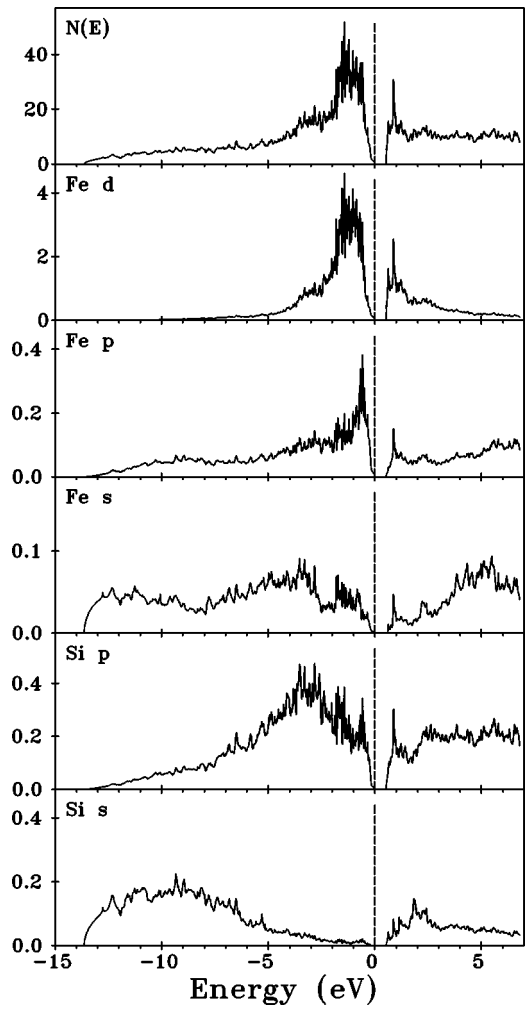


FIG. 3. Self-consistent total density of states $N(E)$ and Fe $s$, $p$, and $d$ and Si $s$ and $p$ partial densities of states. Units are states/(cell eV) or states/(atom eV).

## III. COMPUTATIONAL DETAILS

We have performed first-principles self-consistent [LDA (Ref. 21)] calculations of the electronic structure using the LMTO ASA method. The combined-correction term was included in the band-structure calculations as well as in the matrix elements in the optical functions.[22,23] A detailed description of the LMTO ASA method, including its application to the electronic structure of compounds, has been given elsewhere.[26–28] We shall therefore give only some details of the calculations here. The calculations for $\beta$-$FeSi_2$ were performed using the crystallographic data from Ref. 29. The orthorhombic unit cell ($a=9.863$ Å, $b=7.791$ Å, and $c=7.883$ Å) contains 48 atoms with only four inequivalent atomic sites: two Fe sites and two Si sites. The self-consistent band-structure calculations were semirelativistic, i.e., all relativistic effects were taken into account except for the spin-orbit coupling. The angular-momentum expansion of the basis functions included $l=3$ for iron and $l=2$ for silicon. The Fe $f$ orbitals have a minor effect on the energy bands $E_n^k$; however, it is necessary to include them because usually the $d \rightarrow f$ oscillator strength is much larger than that for the $p \rightarrow d$ or $s \rightarrow p$ transitions. The $k$ integrated functions were evaluated by the tetrahedron method[30] on a grid of

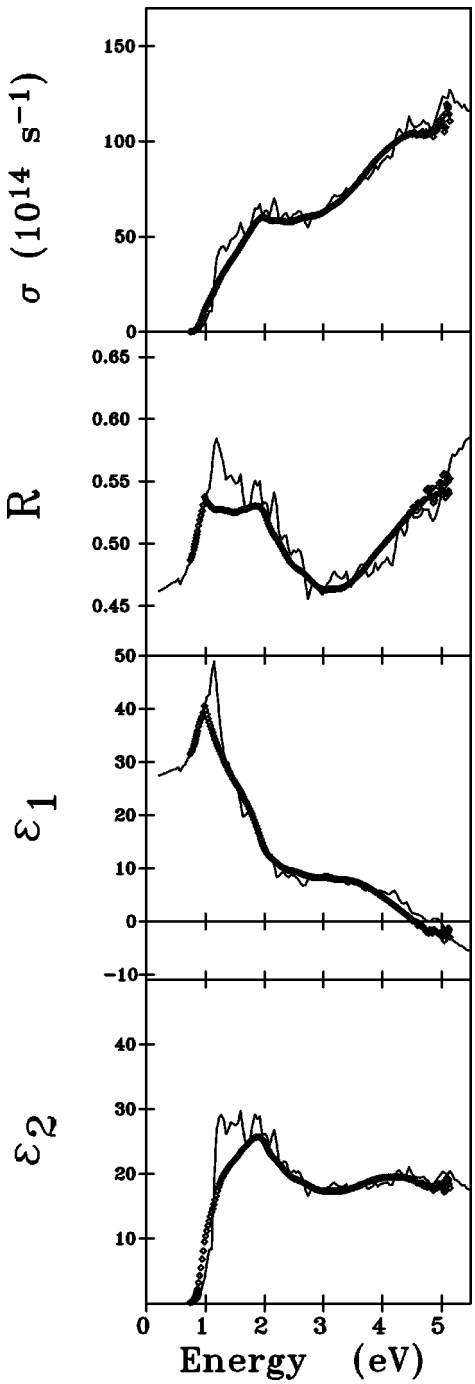


FIG. 4. Comparison between the experimental (circles) and calculated (solid line) optical conductivity $\sigma(\hbar\omega)$, reflectivity $R$, real part $\varepsilon_1(\hbar\omega)$, and imaginary part $\varepsilon_2(\hbar\omega)$ of the dielectric function of $\beta$-$FeSi_2$.

1183 $k$ points in the irreducible part of the Brillouin zone. From the energy bands and the LMTO eigenvectors, we calculated the total and orbital (✓) projected density of states (DOS) and the optical functions ($R$, $\sigma$, $\varepsilon_1$, and $\varepsilon_2$). The method of calculation of the optical properties used here is described in detail in Ref. 2.

## IV. ENERGY BANDS AND DENSITY OF STATES

The energy-band structure of $\beta$-$FeSi_2$ is shown in Fig. 2. We found an indirect gap of 0.44 eV between the $\Gamma$ point and a point located at $\frac{2}{3}(\Gamma$-Z) that agrees with the calculation of Eppenga,[18] but is about 0.4 eV smaller than the experimental value quoted in Refs. 11–14. At $\Gamma$ the direct gap is 0.52 eV. The band structure of $\beta$-$FeSi_2$ is rather complicated; however, it may be understood from the total and partial DOS's presented in Fig. 3. The bands in the lowest region between $-13.5$ and $-5$ eV (relative to the Fermi energy $E_F=0$ eV) have mostly Si $s$ character with some amount of Fe $sp$ character mixed in. Between $-5$ and $-1$ eV the Si $p$ states hybridized with the Fe $d$ states with $t_{2g}$ character, thus forming strong bonding orbitals in the Fe-Si directions. The remaining Fe $d$ states with $e_g$ character are located above and below $E_F$ and they are also strongly hybridized with the Si $p$ states.

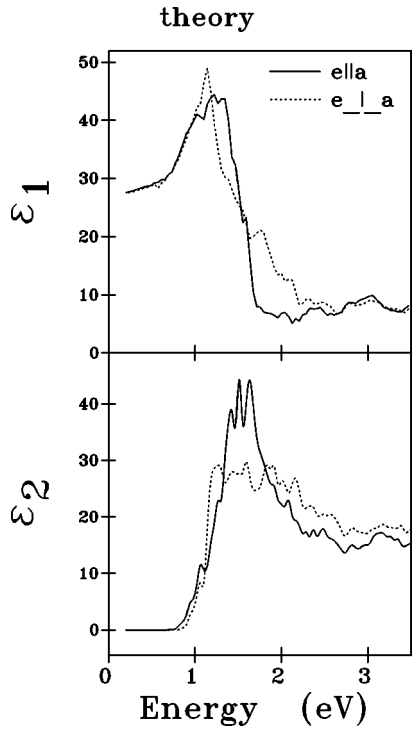


FIG. 5. Calculated real and imaginary parts of the dielectric function for two different polarizations.

## V. CALCULATED OPTICAL PROPERTIES AND COMPARISON WITH EXPERIMENTAL DATA

The linear response of a system to an external electromagnetic field in the long-wavelength limit is determined by the imaginary part $\varepsilon_2(\hbar\omega)$ of the complex dielectric function. We have calculated the dielectric function for frequencies well above those of the phonons and therefore only considered electronic excitations. We used the random-phase approximation and neglected local-field and finite lifetime effects.[31] We first calculated directly the imaginary part of the dielectric function in a wide energy range from 0 to 36 eV. A simple average over polarizations was then performed before the real part of the dielectric function was calculated from the Kramers-Kronig relation.[2] In Fig. 4 we compare the calculated optical conductivity $\sigma(\hbar\omega)$, the reflectivity $R(\hbar\omega)$, $\epsilon_1(\hbar\omega)$, and $\epsilon_2(\hbar\omega)$ with the experiments for thin films. As may be seen, theory and experiment agree in detail with each other. There is a small shift of 0.2 eV of the main

peak of $\epsilon_1(\hbar\omega)$ and $R(\hbar\omega)$ between theory and experiment.

The measurements on a thin film directly from the vacuum chamber, i.e., without any oxide, are in better agreement with theoretical calculations than previously published data. The experimental optical constants for $\beta$-$FeSi_2$ epitaxial layers published in Ref. 32 are in very good correspondence with our data if a $SiO_2$ oxide film of 2 nm thickness is assumed on the surface of their layers.

Strong optical absorption started at 0.8 eV. The small value of the oscillator strength from the gap energy (0.52 eV) to 0.8 eV is due to the fact that the states at the top of the valence bands and at the bottom of the conduction bands consist mainly of Fe *d* states with only a small admixture of Fe *p* and Si *p* states.

Linear extrapolation of the $\epsilon_2^2(\mathrm{E})$ values to $\epsilon_2^2=0$ yields a value of 0.89 eV for the lowest direct transition.[33] This direct-gap value was verified by reflection and transmission measurements. The high level of extrinsic absorption ($10^3-10^4\ \mathrm{cm}^{-1}$) below this photon energy would mask any transitions of low oscillator strength. Single-crystal samples of high quality would be needed to clear up this point.

Figure 5 shows $\epsilon_1(\hbar\omega)$ and $\epsilon_2(\hbar\omega)$ of $\beta$-$FeSi_2$ for the two light polarizations $E \parallel a$ ($a$ is the longest edge of the orthorhombic cell) and $E \perp a$. It should be mentioned that the anisotropy of the optical functions in $\beta$-$FeSi_2$ in the energy range 1–3.5 eV is not as strong as in $WSi_2$ (Ref. 2) and $Pd_2Si$.[3] Preliminary measurements on a $\beta$-$FeSi_2$ single crystal also show a weak anisotropic response.[34]

## VI. CONCLUSION

We have presented reflectance and spectroscopic ellipsometry measurements on high-quality epitaxial films and LDA calculations with the LMTO method of the reflectivity, the optical conductivity, and the complex dielectric function of orthorhombic $\beta$-$FeSi_2$ in a wide energy range and for light polarizations parallel and perpendicular to the crystallographic *a* axis. Excellent agreement is found between measurements and the LDA theory. We observe some anisotropy in the optical functions; the spectra were, however, much more isotropic than the spectra from other transition-metal silicides.

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