Evidence for an indirect gap in β-$FeSi_2$ epilayers by photoreflectance spectroscopy

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Photoreflectance spectra obtained from epitaxial films of semiconducting β-$FeSi_2$ exhibit complex line shapes resulting from a variety of optical transitions. While we have previously established a direct gap at 0.934 ± 0.002 eV at 75 K, we find an additional weak structure at a lower energy. We attribute the origin of this spectral feature to indirect transitions assisted by the emission of a phonon. From our analysis, we determine an indirect gap energy of 0.823 ± 0.002 eV at 75 K. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2936076]

Semiconducting iron disilicide (β-$FeSi_2$) is unique among the transition metal silicides in that it is the only reported light emitter in this family of materials. As a result, considerable attention has been directed to the investigation of the optical and structural properties of β-$FeSi_2$ and the impact of various growth techniques. Since the beta phase can be viewed as a moderate distortion of the CaF_2 structure by way of the Jahn–Teller effect,[1] this results in a material whose band structure and consequent optical properties are strongly influenced by slight lattice distortions.[2] Observations of luminescence at 1.5 μm have been reported from β-$FeSi_2$ grown by various techniques.[3–7] However, luminescence is not guaranteed, and its origin is still uncertain. In fact, the nature of the energy gap (direct or indirect) is also not well determined. It is likely that both the luminescence and the functional energy gap are strongly influenced by perturbations of the band structure due to lattice strain,[8] impurities, and/or defects.[9]

In this study, we present photoreflectance (PR) spectra obtained from a molecular beam epitaxy (MBE) grown film and single crystal of β-$FeSi_2$. The spectra exhibit complex line shapes resulting from a variety of optical transitions. For both the epitaxial film and crystal, the main spectral features can be described by direct transitions involving the ground and first excited state of the free exciton.[10] In addition, the MBE film spectrum shows other weak features. These have been attributed to an impurity (0.904 eV) and bound exciton (0.914 eV) transitions.[10] Futhermore, it is important to note that an observed redshift of the direct transitions of the MBE film relative to the single crystal strongly suggest that the surface of the epitaxial film is under tensile stress.[10] In this paper, we report a new weaker resonance at even lower energies which we attribute to an indirect transition assisted by the emission of a phonon.

PR spectroscopy is a very powerful technique for investigating optical transitions in bulk semiconductors and their microstructures.[11,12] Its ability to resolve critical point transitions is excellent; as such, PR is a technique immediately applicable to materials with complex electronic structure such as β-$FeSi_2$. In addition, the theory for connecting measured spectral line shapes to material parameters is well developed.[11]

PR spectra were acquired using an automated PR system,[13] equipped for providing sample temperatures from 12 to 350 K. Data were collected over a spectral range of 0.80–1.15 eV with an energy resolution of 5 meV. The pump source was a 635 nm laser diode modulated at a frequency of 1000 Hz. The average power density of the pump source at the sample surface was 35 mW/cm^2. The detector was a thermoelectrically cooled InGaAs photodiode.

The epitaxial β-$FeSi_2$ film investigated in this work was grown in an ultrahigh vacuum MBE chamber using a template technique.[14] The Fe and Si were coevaporated in a ratio to achieve a stoichiometric compound with a film thickness of about 250 nm. The substrate was an *n*-type single crystal Si (100) wafer with a resistivity of 1–5 $k\Omega$ cm. The β-$FeSi_2$ single crystal investigated in this work was grown by chemical vapor transport in closed ampoules using iodine as the transporting agent. They have a needlelike shape with dimensions of approximately $(5-10) \times 2 \times 0.5$ mm^3 and have n-type conductivity. For both the epitaxial and single crystal samples, the PR measurements were taken on the β-$FeSi_2$ (100) surfaces. Details of epitaxial and single crystal growth can be found in Refs. 15 and 16, respectively.

PR spectra taken at 75 K on both the MBE and single crystal samples are shown in Fig. 1. The 18 meV redshift of the MBE spectrum, resulting from tensile stress, was determined by PR line shape analysis.[10] In this work, we direct our attention to the weak spectral feature (at ~0.85 eV) observed at lower energies in the MBE samples. It is important to note that this weak feature is not observed in our single crystal samples, but can be described energetically by an indirect transition to the excitonic ground and first excited state via the emission of a phonon. This is analogous to the observation of direct transitions to excitonic states,[10] resulting in the main spectral feature seen in Fig. 1 and in absorp-

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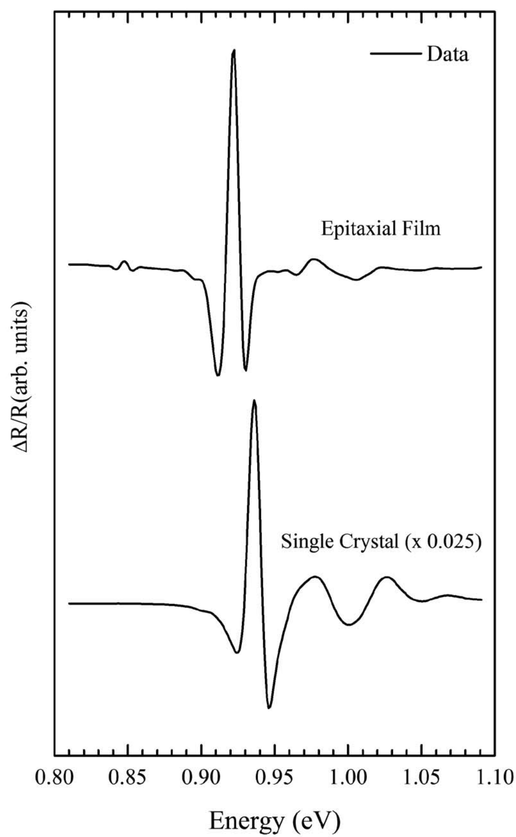

FIG. 1. PR specta taken at 75 K on a $\beta-FeSi_2$ epitaxial film (top) and bulk single crystal (bottom).

tion spectra of these samples.[17] Normally indirect transitions are not observable in PR spectroscopy. However, these indirect features are observable in PR due to back-surface relection from the $\beta-FeSi_2/Si$ interface (see Ref. 11 p. 559 for additional discussion and references).

The PR spectra were fitted by a least-squares algorithm to a generalized Lorentzian line shape of the form[11,18]

$$\frac{\Delta R}{R}(E) = \mathrm{Re}\left[\sum_{j=1}^{n} C_j e^{i\theta_j}(h\nu - E_j + i\Gamma_j)^{-m}\right], \qquad (0.1)$$

where C_j and θ_j are the amplitude and phase of the line shape and E_j and Γ_j are the energy and broadening parameter of the interband transitions. The exponent m depends on the type of critical point transition, i.e., band-to-band, excitonic, and others.[11]

The weak transition can only be fit using two excitonic Lorentzian line shapes; one line shape is not sufficient to describe this spectral feature. This is the same argument that was used to demonstrate the presence of the ground and first excited states of the direct gap excition in our earlier paper.[10] The experimental result and the line shape fit are shown in Fig. 2. The line shape parameters are given in Table I.

We compare our results with the optical absorption results of Udono *et al.* on unstrained, thick single crystal samples.[19] They also find evidence of an indirect transition, and derive an energy of 31 meV for the dominant phonon that is in excellent agreement with earlier results.[20] They determined the indirect exciton ground state energy at 70 K to be 0.810 eV.

From our fitting, we calculate transitions at $E_{ex1}^{ind} = 0.845 \pm 0.002$ eV and $E_{ex2}^{ind} = 0.852 \pm 0.002$ eV that we take

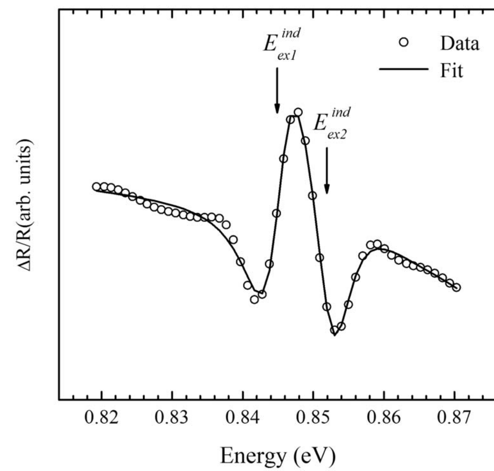

FIG. 2. Expanded view of the PR spectrum (dotted curve) of the $\beta-FeSi_2$ epitaxial film in the energy region of the weak transition. The corresponding theoretical fit is represented by the solid curve.

to be the ground and first excited state respectively of the indirect exciton. This yields a binding energy of $E_{BE}^{ind} = 0.009 \pm 0.002$ eV. From this binding energy and the dominant phonon energy cited above, the value of the indirect energy gap is determined to be $E_g^{ind} = 0.823 \pm 0.002$ eV at 75 K. If the exciton binding energy is added to the ground state energy obtained by Udono *et al.* the indirect band gap is found to be 0.819 eV, which compares well with our value of 0.823 ± 0.002 eV. These results are tabulated in Table I. The slight blueshift of our value can be attributed to tensile stress, which has been shown by Miglio and Meregalli[2] to produce a small blueshift in the indirect gap and a much larger redshift in the direct gap. As discussed previously, the redshift of the MBE spectrum vis-á-vis the single crystal spectrum is clearly illustrated in Fig. 1.

PR spectra obtained from an epitaxial film and bulk single crystal of $\beta-FeSi_2$ exhibit complex line shapes resulting from a variety of optical transitions. For both the thin film and single crystal, the main spectral features have previously been described by direct transitions involving the ground and first excited state of the free exciton. The new result is the observation of a weak lower energy feature in the PR spectrum of the thin film sample. This weak feature was found to be composed of phonon-assisted indirect transitions involving the ground and first excited state of the free exciton. The indirect gap of this MBE grown $\beta-FeSi_2$ epitaxial film was determined to be 0.823 ± 0.002 eV at 75 K.

TABLE I. PR results obtained on epitaxial films of semiconducting β-$FeSi_2$ at 75 K. E_{ex1}^{ind} and E_{ex2}^{ind} denote the transition energies of the ground state and first excited-state of the free exciton, respectively. E_g^{ind} is the indirect energy gap, and E_{BE}^{ind} is the free exciton binding energy. C_j and Γ_j are the amplitude and broadening parameters of Eq. (1). The uncertainty in the energies is ± 0.002 eV.

Technique	Transition	Energy (eV)	C_j ($\times 10^{-6}$)	Γ_j (meV)
PR	E_{ex1}^{ind}	0.845	0.75	4.45
(T=75 K)	E_{ex2}^{ind}	0.852	0.64	4.58
	E_{BE}^{ind}	0.009		
	E_g^{ind}	0.823		

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