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Nature of the band gap of polycrystalline β-$FeSi_2$ films

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We present experimental evidence for the indirect nature of the β-$FeSi_2$ gap. We furthermore show, by analyzing the temperature dependence of the direct gap by means of a thermodynamic empirical model, that β-$FeSi_2$ exhibits an unusually strong electron-phonon interaction. We finally deduce the electron-hole mobility from our measurements.

Thin films of metal silicides have been widely studied for many years because of the large number of potential applications in electronics such as Schottky barriers and Ohmic contacts.[1] Recently, increasing interest has been devoted to another family of silicides: the semiconducting transition-metal silicides. The interest is based on the possibility to combine their optoelectronic properties with the well-developed silicon technology. In particular, among the semiconducting transition-metal disilicides, $FeSi_2$ shows a stable orthorhombic semiconducting phase, the so-called β phase, for temperatures below 930 °C, after which it changes to a tetragonal metallic phase.[2] The structural properties of β-$FeSi_2$ have been extensively studied by means of several techniques. Depending on the growth process, the crystalline quality can vary greatly. Up to now, epitaxial films of thickness up to 30 nm have been obtained on (111) Si substrates by solid-state epitaxy (SPE).[3,4] Above this thickness polycrystalline films are obtained. The nature of the gap, i.e., direct or indirect, of β-$FeSi_2$ is still an open question. In the past years, Bost and Mahan[5] and Dimitriadis *et al.*[6] ascribed their observations, obtained by linear transmittance measurements and by photodeflection spectroscopy, respectively, to a *direct gap* with a magnitude of 0.85–0.87 eV at room temperature (RT). However, a recent theoretical work describes β-$FeSi_2$ in terms of an indirect gap only about 35 meV lower than the direct gap at $T=0$ K.[7]

In this paper we present experimental evidence of the existence of an indirect gap at low temperatures, slightly lower in energy than the direct one. Optical linear transmittance measurements have been performed on polycrystalline samples, 450 nm thick. Furthermore, the dependence of the direct gap on temperature is investigated. Analyzing the observed dependence by means of a thermodynamic empirical model reveals a strong electron-phonon coupling and provides, in addition, an estimate of the electron-hole mobility.

The samples have been prepared by annealing of an iron film deposited on Si(111) at a temperature of 620 °C. They have been proven by previous x-ray experiments to be polycrystalline single-phase β-$FeSi_2$.[4] For optical absorption, the sample was mounted on the cold finger of a closed cycle helium cryostat. The measurements were taken over a wide range of temperature from 10 K to RT using a chopped tungsten lamp, with optical fiber delivery, as excitation source. The dispersive system consisted of an IR grating blazed at 1 μm with a linear reciprocal dispersion of 16 Å/mm in the 0.6–2 μm range. The dispersed radiation was detected by a Ge photodiode and measured by a lock-in amplifier.

Figure 1 shows the absorption spectra at different temperatures. Theoretically, the dependence of the absorption coefficient $\alpha(\hbar\omega)$ on the energy of the incoming photon $\hbar\omega$ is given by[8]

$$\alpha(\hbar\omega)=A(\hbar\omega-E_g^d)^{1/2} \qquad (1)$$

in the case of a direct gap and by

$$\alpha(\hbar\omega)=A'(\hbar\omega-E_g^{\mathrm{ind}}-E_{\mathrm{ph}})^2 \qquad (2)$$

in the case of an indirect gap, with the creation of a phonon with energy E_{ph}. A' contains the probability of phonon emission, E_g^{ind} and E_g^d are the magnitude of the indirect gap and the direct gap, respectively, and A is a constant if direct transitions are allowed. According to the calculations of Christensen,[7] at the Γ point, the valence band has 11% Fe p character and the conduction band has 23.6% Fe d character, therefore allowing the direct transition. Momentum-conserving transitions between parabolic bands then result in an absorption proportional to the square root of the photon energy, above the energy gap. One expects no absorption below the energy gap and, therefore, a steeply rising absorption edge. On the contrary, our data show a long tail below the edge and above 80 K also a significant shoulder superimposed on the tail. Below 80 K the spectra can be described by a direct gap

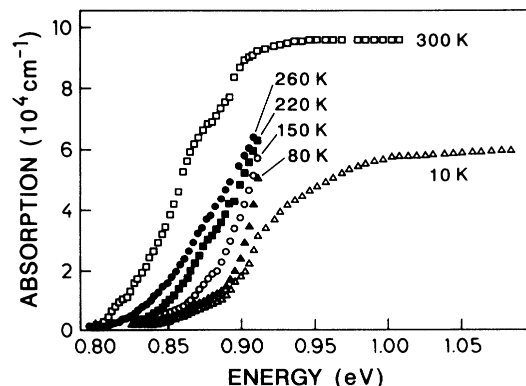

FIG. 1. Absorption spectra of a polycrystalline film grown on Si(111) substrate at different temperatures.

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around 0.9 eV and an indirect gap a few tens of meV below the direct one.

Figures 2 and 3 show, respectively, the spectra at 10 and 80 K fitted using the relation (1) near the edge at 0.9 eV and the relation (2) in the low-energy part of the spectra, corresponding to the tail. The energy values extrapolated to $\alpha=0$ are

$$E_g^{\mathrm{ind}}+E_{\mathrm{ph}}\sim 0.84\ \mathrm{eV},\quad E_g^d\sim 0.89\ \mathrm{eV}\ \text{at}\ 10\ \mathrm{K},$$

$$E_g^{\mathrm{ind}}+E_{\mathrm{ph}}\sim 0.83\ \mathrm{eV},\quad E_g^d\sim 0.90\ \mathrm{eV}\ \text{at}\ 80\ \mathrm{K}.$$

Therefore, at least for these temperatures, there is clear evidence of the existence of an indirect gap at a slightly lower energy than the direct one. At higher temperatures, the indirect gap behavior is well described by two linear dependences: one for phonon absorption and one for phonon creation, yielding, by extrapolation to $\alpha=0$, the values of $E_1=E_g^{\mathrm{ind}}-E_{\mathrm{ph}}$ and $E_2=E_g^{\mathrm{ind}}+E_{\mathrm{ph}}$. However, above 80 K, the shoulder developing on the intrinsic absorption spectrum shows the presence of an additional absorption mechanism, which is apparently temperature activated, and is therefore ascribed to extrinsic transitions involving defect states within the forbidden gap. Intrinsic grain boundary states are suspected to be present below the gap due to the polycrystalline nature of the samples investigated. These states cause a band tailing of the gap. Band tails in polycrystalline Si have been attributed to short-wavelength potential fluctuations due to spatial disorder.[9] These quantum-well fluctuations result in free-carrier localization. This effect could be the origin of the temperature-activated process below the gap, measured in our samples. This latter process is hard to deconvolute from the spectra. It is thus not possible to determine the exact value of E_g^{ind}, usually obtained as the average of E_1 and E_2. We show in Fig. 4 the values for E_2 evaluated by the spectra up to 80 K (crosses). However, we can determine the direct energy gap E_g^d by applying Eq. (1) to the spectra in the region of the edge. This can be done for the whole temperature range from 10 to 300 K.

Figure 4 shows the dependence of the direct gap as a function of the temperature (solid circles). The solid line is the calculated dependence following a recent thermodynamical model[10] described by the equation

$$E_g^d(T)=E_g(0)-S\langle\hbar\omega\rangle\left[\coth\left(\frac{\hbar\omega}{2kT}\right)-1\right], \tag{3}$$

where $E_g(0)$ is the energy gap a 0 K, $\langle\hbar\omega\rangle$ is an average phonon energy, and S is a dimensionless constant related to the electron-phonon coupling. This relation has been used successfully to describe the temperature dependence of the gap in Si, GaAs, GaP, and C.[10] The fit gives the values of the parameters S, $\langle\hbar\omega\rangle$, and $E_g(0)$. In the case of polycrystalline β-$FeSi_2$, we obtain $S=6.22$, $\langle\hbar\omega\rangle=71$ meV, and $E_g(0)=0.90$ eV.

Comparing the electron-phonon coupling parameter $S=6.22$ evaluated for β-$FeSi_2$ with the values calculated by O'Donnell and Chen[10] for Si ($S=1.49$), GaAs ($S=3.00$), GaP ($S=3.35$), and C ($S=2.31$), it is surprisingly much greater. From Eq. (3), for $kT\gg\langle\hbar\omega\rangle$,

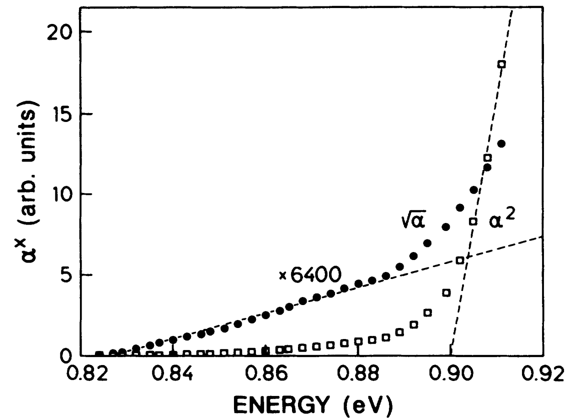

FIG. 3. Square root of the absorption coefficient (solid circles) and square of the absorption coefficient (open squares) at 80 K as a function of the photon energy. The solid lines show the fit of relation (1) to α^2 and (2) to $\alpha^{1/2}$.

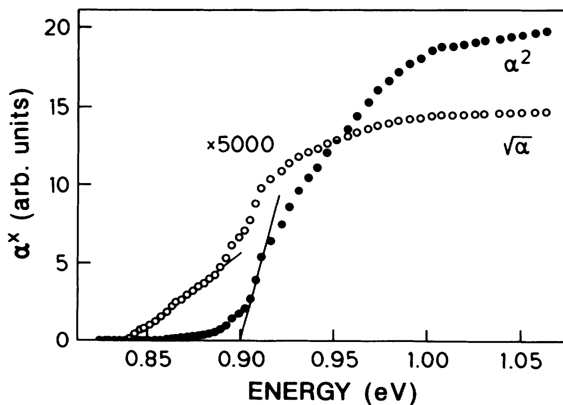

FIG. 2. Square root of the absorption coefficient (open circles) and square of the absorption coefficient (solid circles) at 10 K as a function of the photon energy. The solid lines show the fit of relation (1) to α^2 and (2) to $\alpha^{1/2}$.

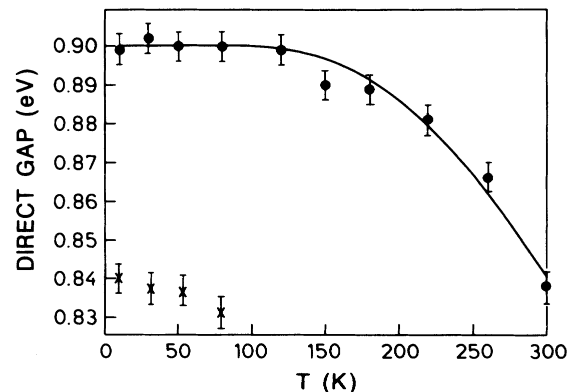

FIG. 4. Temperature dependence of the direct gap: The solid circles are the experimental results and the solid line is the calculated dependence according to Eq. (3). The low-temperature dependence of the indirect gap, overestimated by the phonon energy, is indicated by the crosses.

$$\frac{dE_g^d(T)}{dT} = -2kS = -1.2\ \mathrm{meV\,K^{-1}}. \quad (4)$$

This strong dependence of the gap on the temperature is justified by the unusually large electron-phonon coupling coefficient. In fact, our experimental finding is in agreement with the calculations of Christensen,[7] who described dE_g^d/dT as consisting of two terms, one caused by lattice vibrations and the second by the static thermal expansion. Within this model, the strong electron-phonon coupling originates predominantly from the lattice distortion, whereas the contribution of the static term is negligible (μ eV K^{-1}). Christensen's calculations are based on the classic work by Fan,[11] who gave, in addition to the explicit expression of dE_g^d/dT, its relation to the carrier mobility μ for the case of strong lattice scattering. Combining the expressions (23) and (25) of Ref. 11, it will follow that

$$\mu = \frac{48}{9\pi}\left(\frac{3}{4\pi}\right)^{1/3}\left(\frac{\pi}{2}\right)^{1/2}\frac{e\hbar^2 k}{(\Omega)^{1/3} m^{*3/2}(kT)^{3/2}\,\partial E_g^d/\partial T}, \quad (5)$$

where Ω is the volume of the unit cell and m^* is the effective mass. We estimated the mobility by assuming a similar effective mass ($m^* = 0.8 m_0$) and a similar interaction parameter for electrons and holes. A mobility of about 13 $cm^2 V^{-1} s^{-1}$ at RT can thereby be deduced. This value is higher than the mobility measured by Dimitriadis *et al.*[6] who showed that the highest mobility corresponds to the lowest growth temperature. Our silicide films were annealed at 620 °C. This probably results in a lower grain boundary density and consequently explains the highest mobility value calculated.

In conclusion, by using optical linear transmittance measurements in the range 0.8–1.0 eV on polycrystalline β-$FeSi_2$ at low temperature, we have demonstrated the presence of an indirect gap a few tens of meV lower than the direct one. At higher temperatures, the contribution of defect levels prevents the determination of the indirect gap value. The temperature dependence of the direct gap has been measured from 10 to 300 K. Analyzing the experimental results with a model describing the temperature dependence of the gap in terms of thermodynamic quantities has allowed us to deduce a strong electron-phonon interaction, in agreement with a recent theoretical work. We finally note that all our results are related to polycrystalline samples. It would be interesting to study epitaxial films where the defect levels, probably connected to grain boundaries, are absent. Work is in progress to prepare thick films of high enough quality in order to carry out this kind of measurement.

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