Photoconductivity in n-type β-$FeSi_2$ single crystals

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Photoconductivity in β-$FeSi_2$ single crystals was observed in the temperature range of 80–250 K. The energy gap, 0.89 eV at 85 K, and its temperature dependence were determined. The values of the average phonon energy, 55 meV, and the electron-phonon coupling parameter, $S=2.75$, were evaluated. The observed quenching of photoconductivity is explained in assuming the two-center model. The donor and acceptor activation energy of 70 and 120 meV, respectively, as well as the hole mobility due to lattice scattering were determined.

Beta-iron disilicide (β-$FeSi_2$) belongs to the family of semiconducting silicides. Due to its direct energy gap,[1] β-$FeSi_2$ has received considerable attention as a very attractive material for light detectors, photovoltaic applications,[2] and for the development of new optoelectronic devices.[3]

The recently reported high value of the Hall mobility (at low temperatures in single crystals the hole mobility is up to 1200 $cm^2/V\,s$,[4] and the electron mobility is up to 48 $cm^2/V\,s$,[5] i.e., up to 25–50 times higher than maximum values previously reported[6–8]) increased interest in this material and the possibility of its application.

Optical absorption measurements on β-$FeSi_2$ revealed the direct transition near 0.83–0.89 eV at room temperature.[1,9–14] There are also indications of an indirect gap of a few tens of meV's lower than the direct one[13,14] and a second higher-energy direct transition at 1.01 eV (Ref. 1) [1.05 eV (Ref. 12)].

The transport properties measurements were performed on n-type β-$FeSi_2$ polycrystalline sintered samples[8] and single crystals.[5] The magnetic-field dependence of the Hall coefficient was observed in the temperature range 30–300 K and explained within the limit of a two-band model.[5] Parameters of charge carriers taking part in conductivity were calculated and the separation between the bands (25 meV) was estimated.[5]

We report now on the results of the photoconductivity (PC) measurements of β-$FeSi_2$. The investigation of photoconductivity allows us to enlarge our knowledge about its band structure. From a technological point of view, photoelectric properties of such a material may lead to some optoelectronic devices that can be integrated into silicon technology.[15]

β-$FeSi_2$ needlelike crystals were grown by chemical vapor transport using iodine as a transport agent.[16] The as-grown undoped crystals show n-type conductivity which may be caused by native defects or iodine impurities. The electrical contacts were made by vacuum evaporation of Au or directly soldering with In.

The resistivity ρ was measured in the temperature range from 30 to 300 K. Photoconductivity measurements were performed using the standard computer-assisted lock-in method in the wavelength range 900–1700 nm (0.75–1.5 eV) in the temperature interval from 80 to 300 K.

A 300 W filament lamp and a grating monochromater were used as a radiation source. The set temperature was computer controlled and permitted to keep the temperature in the range 80–300 K within an accuracy of 0.2 K or to perform a slow temperature scan within the same temperature region with a given rate.

Transport properties of the samples studied were reported earlier.[5] A typical variation of resistivity vs temperature is presented in Fig. 1. The resistivity is about 3–5 Ω cm at room temperature, shows a minimum near 200 K, and increases with decreasing temperature.

The normalized PC spectra of β-$FeSi_2$ measured at different temperatures are given in Fig. 2. Five peaks and features at $h\nu_1=0.86$ eV, $h\nu_2=0.94$ eV, $h\nu_3=0.99$ eV, $h\nu_4=1.07$ eV, and $h\nu_5=1.27$ eV can be observed.

Taking into account that near the fundamental absorption edge the PC signal is proportional to the absorption coefficient α and is due to direct optical transitions[1,9–12] it can be written that

$$\Delta\sigma \propto \alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}, \tag{1}$$

where A is a constant and E_g is the width of the energy gap. The E_g value estimated according to the dependence $(\Delta\sigma h\nu)^2$ vs $h\nu$ is equal to 0.89 eV at 85 K and decreases with increasing temperature (Fig. 3). The value of the energy gap at room temperature determined by the $E_g(T)$ dependence extrapolation is about of 0.85 eV,

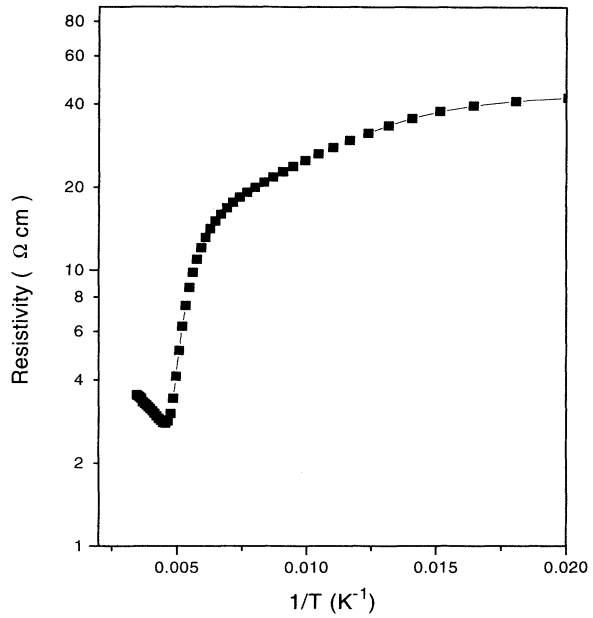

FIG. 1. Dependence of resistivity vs $1/T$.

which is in good agreement with Refs. 10–12 and 14.

The temperature dependence of the direct gap was analyzed on the basis of the equation[17]

$$E_g(T)=E_g(0)-S\langle E_{\rm ph}\rangle\left[\coth\left\{\frac{\langle E_{\rm ph}\rangle}{2kT}\right\}-1\right], \quad (2)$$

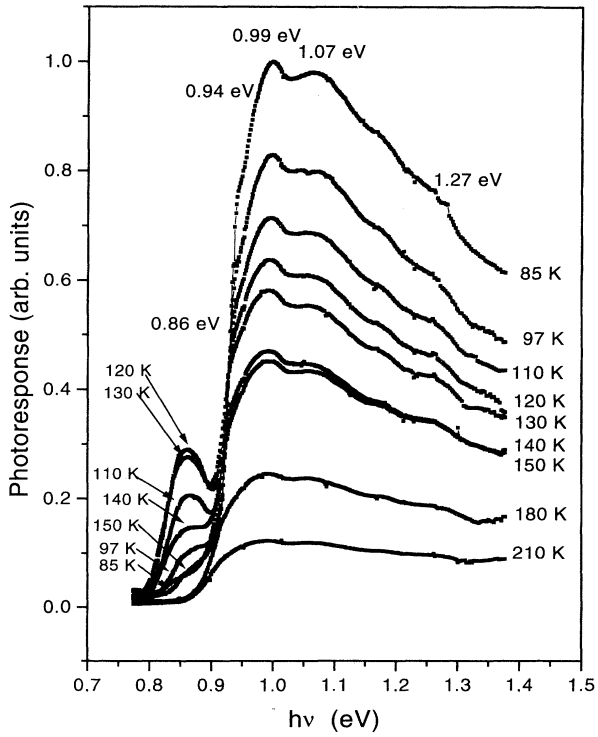

FIG. 2. Photoconductivity spectra of β-$FeSi_2$ at different temperatures.

where $E_g(0)$ is the band gap at zero temperature, $\langle E_{\rm ph}\rangle$ is an average phonon energy, and S is a dimensionless constant related to the electron-phonon coupling.

Equation (2) was used for the first time to describe the temperature dependence of the gap in Si, GaAs, GaP, and diamond[17] and fit measured values excellently. By fitting our data (Fig. 3) to Eq. (2) the following set of parameters were obtained: $E_g(0)=0.894$ eV, $\langle E_{\rm ph}\rangle=55\pm3$ meV, and $S=2.75\pm0.25$. Comparison of our data with those of Giannini *et al.*[14] shows that our $E_g(0)$ coincides with their data (0.90 eV), our $\langle E_{\rm ph}\rangle$ is about 30% lower than their value ($\langle E_{\rm ph}\rangle=71$ meV[14]), and our S is more than two times smaller [$S=6.22$ (Ref. 14)]. Our value of the electron-phonon coupling parameter exceeds the reported value for Si [$S=1.49$ (Ref. 17)] and is similar to those of diamond ($S=2.31$), GaAs ($S=3.00$), and GaP ($S=3.35$).[17]

It is worth mentioning that our data and the data of Giannini *et al.*[14] are related to single crystals and polycrystalline films, respectively. The latter could be influenced in particular by the defect levels, probably connected to grain boundaries.[14]

From Eq. (2) we can write

$$\frac{dE_g}{dT}=-\frac{S\langle E_{\rm ph}^2\rangle}{2kT^2\sinh^2(\langle E_{\rm ph}\rangle/2kT)}\ . \quad (3)$$

At high temperatures, $kT\gg\langle E_{\rm ph}\rangle$ and the slope of the E_g vs T curve approaches the limiting value

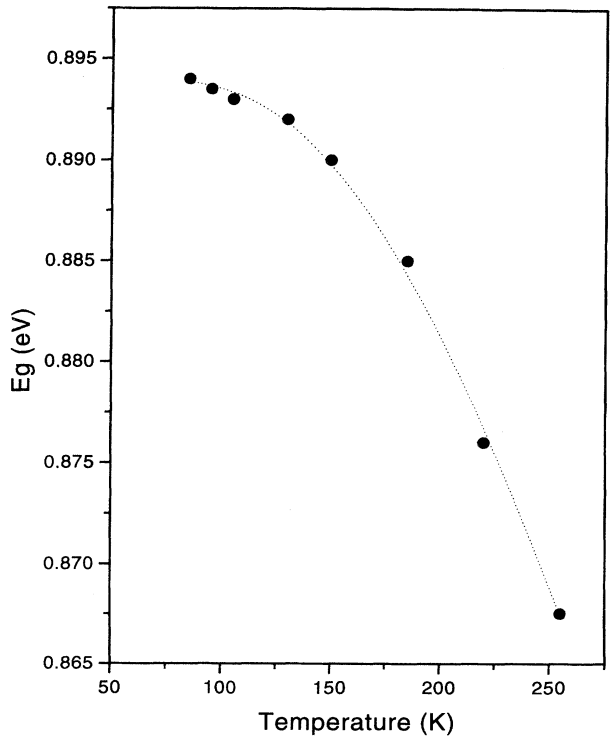

FIG. 3. Temperature dependence of the direct band gap of β-$FeSi_2$. The solid circles are the experimental results and the dotted line is the calculated dependence according to Eq. (2).

$$\left[\frac{dE_g}{dT}\right]_{\max} = -2Sk \ . \tag{4}$$

The calculated value of $(dE_g/dT)_{\max}$ is equal to $(-0.48$ meV/K). It is in good agreement with the value $(-0.45$ meV) determined by Waldecker, Meinhold, and Birkholz[18] at high (700–1200 K) temperatures and confirm the strong interaction between the band-edge states and the phonon system in β-$FeSi_2$ predicted by Christensen.[19]

Assuming that the mobility μ is determined by acoustic phonon scattering, the value of μ is given by[14,20]

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

where Ω is the volume of the unit cell and m^* is the effective mass.

The temperature dependence of the hole mobility was calculated in accordance with Eqs. (4) and (5), using the obtained values of S and $\langle E_{\rm ph}\rangle$ and assuming that $m_p^*/m_0 = 1.0$.[4] At room temperature the value of the hole mobility is about 31 $cm^2/V\,s$, which is in agreement with the previously reported data of the Hall mobility [10–40 $cm^2/V\,s$ (Refs. 4 and 21)] and increase with decreasing temperature (Fig. 4). A good agreement observed between the calculated and experimental dependence of $\mu(T)$ leads to the conclusion that the phonon scattering dominates in p-type β-$FeSi_2$ single crystals in the temperature range of about 120–300 K (Fig. 4). Similar analysis of the electron mobility in n-type β-$FeSi_2$ single crystals is more complicated because its transport properties are determined by two charge carriers.[5]

The observed photoconductivity spectra show a fine structure (Fig. 2). Identification of these maxima requires knowledge of the energy band structure of β-$FeSi_2$. The calculation of the electronic band structure of the compound studied was performed by Christensen.[19]

Shoulder 2 and peak 3 ($\Delta h\nu_{23} = 0.05$ eV) could be ascribed to the interband transitions involving both conduction bands of the β-$FeSi_2$ crystal. The value (50 meV) is in satisfactory agreement with the calculated value of the separation between the two conduction bands (35 meV[19]). The features at $h\nu_4$ and $h\nu_5$ can be explained as a result of the interband transition involving deeper valence band states.[19]

The temperature dependence of the photocurrent spectral peak $h\nu_1$ exhibits a maximum at 125 K (Fig. 5). It can be explained on the basis of a two-center model, i.e., a model in which two recombination centers are present with markedly different capture coefficients for at least one of the carriers.[22,23] We assume the existence of both a donor level and an acceptor level in the n-type β-$FeSi_2$ crystal studied. The donor-like level provides the photocurrent temperature increasing. Its activation energy

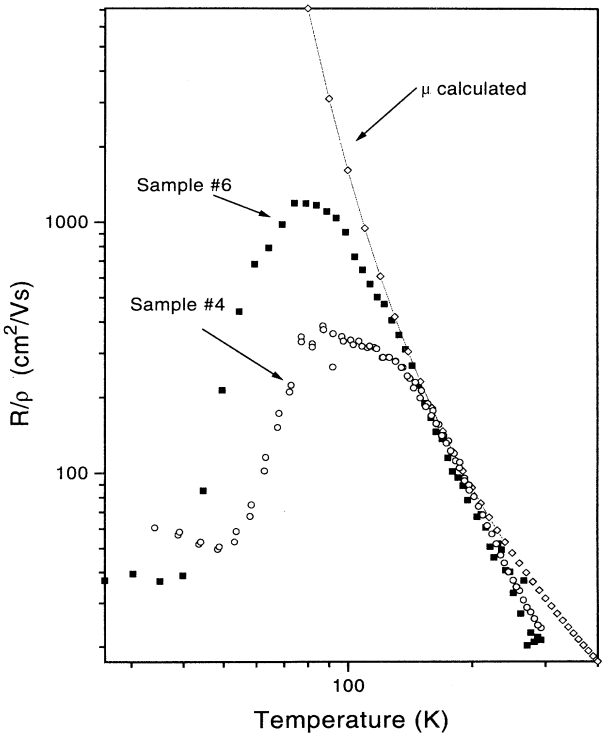

FIG. 4. Temperature dependence of R/ρ of p-β-$FeSi_2$. The open circles (sample No. 4) and the solid squares (sample No. 6) are the experimental results taken from Ref. 4. The solid curve is the calculated dependence according to Eq. (5).

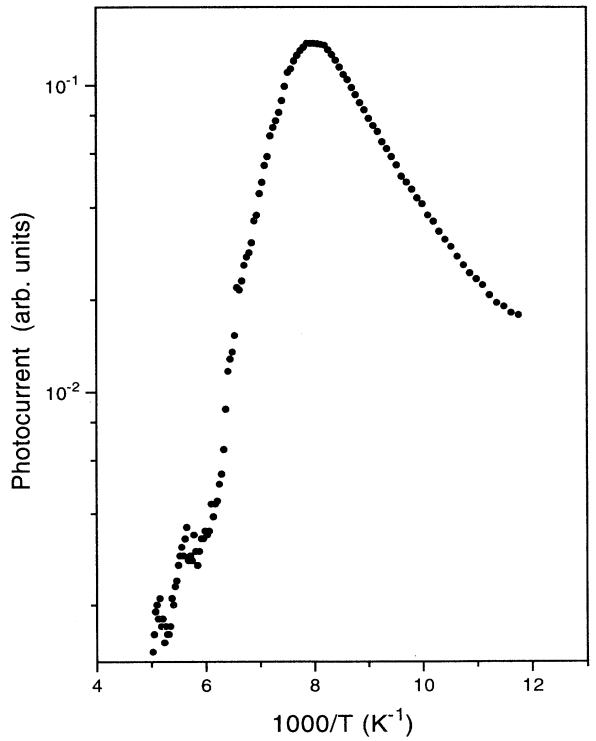

FIG. 5. Photocurrent temperature dependence at $h\nu_1 = 0.86$ eV.

calculated from the slope of the dependence ln(photocurrent) vs $1/T$ at $T < 120$ K is about 0.07 eV. The acceptor level which is responsible for the trapping processes of photoexcited carriers and hence for the photocurrent quenching processes is deeper (0.12 eV). The obtained value is similar to that determined from the results of transport measurements on p-type β-$FeSi_2$ [0.10 eV (Ref. 4)]. A more detailed analysis of the photoconductivity spectra would be difficult to carry out in the framework of the available theoretical calculation of the energy band structure of β-$FeSi_2$.

In summary, the photoconductivity in β-$FeSi_2$ single crystals was observed between 80 and 250 K and reveals a fine structure. The temperature dependence of the energy gap, the values of the average phonon energy and the electron-phonon coupling parameters, the activation energy of donors and acceptors, as well as the hole mobility due to lattice scattering were determined.

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