Indirect optical absorption of single crystalline β-$FeSi_2$

Haruhiko Udono[a] and Isao Kikuma
College of Engineering, IBARAKI University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan

Tsuyoshi Okuno and Yasuaki Masumoto
Institute of Physics, University of Tsukuba, 1-1-1 Tennohdai, Tsukuba, Ibaraki 305-8573, Japan

Hiroyuki Tajima
Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

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We investigated optical absorption spectra near the fundamental absorption edge of β-$FeSi_2$ single crystals by transmission measurements. The phonon structure corresponding to the emission and absorption component was clearly observed in the low-temperature absorption spectra. Assuming exciton state in the indirect allowed transition, we determined a phonon energy of 0.031 ± 0.004 eV. A value of 0.814 eV was obtained for the exciton transition energy at 4 K. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1790590]

β-$FeSi_2$ is increasingly attracting attention as a suitable material for use in silicon-based optoelectronic devices, due to its band gap being near the absorption minimum of quartz fibers optical.[1,2] Recently Leong *et al.* and Suemasu *et al.* fabricated light-emitting diodes operating at the wavelength of 1.5–1.6 μm by introducing β-$FeSi_2$ particles into a silicon bipolar junction.[3,4] Chu *et al.* also demonstrated the 1.57 μm electroluminescence (EL) at room temperature from sputter-deposited β-$FeSi_2$ films on Si.[5] However, the luminescence mechanism in β-$FeSi_2$ is not clearly understood, because the electronic structure of β-$FeSi_2$ is not clarified yet. The band-gap nature, i.e., a direct or indirect gap, is also still controversial.

A number of experimental studies on the band-gap nature of β-$FeSi_2$ have been performed by optical absorption measurements. From the analysis of the energy dependence of the absorption coefficient, in most reports it is argued that β-$FeSi_2$ has a direct band gap,[1,2,6–12] but a few papers report an indirect gap lower than the direct one by some tens of meV.[13–15] The reported values of the band gap are 0.80–0.95 eV for direct gap and 0.7–0.78 eV for the indirect one. The wide variation of the reported values suggests some uncertain factors existed in measured samples.

In order to study the band-gap nature, optical transmission measurement using thick single crystalline samples is preferable because the absorption coefficient of crystals with an indirect energy gap is usually low. Recently, we have succeeded in growing large-sized β-$FeSi_2$ single crystals. In this letter, we report optical transmission measurements of β-$FeSi_2$ single crystals.

Single crystalline β-$FeSi_2$ ingots were grown by the temperature gradient solution growth (TGSG) method using Ga solvent. Details of the growth condition were described elsewhere.[16–18] The crystals showed *p*-type conduction with a typical hole concentration of 1.5×10^{19} cm^{-3} at 300 K and less than 1×10^{16} cm^{-3} at 25 K. Crystals cut from grown ingots were ground using carborundum and polished using colloidal alumina. After the polishing, the surface of the crystals showed a mirrorlike face. Optical transmission spectra were measured between 3.5 and 300 K using double-beam spectrophotometer (Hitachi U-4000). Reflection measurements were made at 300 K using a UV-VIS-NIR microspectrophotometer (Nippon Bunko). The absorption coefficient α was obtained by solving the following equation, assumed that the temperature dependence of reflectivity R was negligible throughout the measured spectra region (0.7–1.0 eV):

$$T = \frac{I_T}{I_T'} = \frac{(1-R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)}, \tag{1}$$

where d is the thickness, I_T is the transmitted intensity, and I_T' is the apparent transmitted intensity.[19]

Figure 1 contains experimental data on the relationship between $\alpha^{1/2}$ and $h\nu$ obtained from transmission measurements on a crystal of thickness 0.0044 cm, recorded at five temperatures between 4 and 300 K. The stepped structure characteristic of the intrinsic absorption edge of crystals with an indirect energy gap was observed in the low-temperature spectra. The energies E_{P1}^e and E_{P1}^a refer to the thresholds for structural components as defined in the 70 K spectrum. The

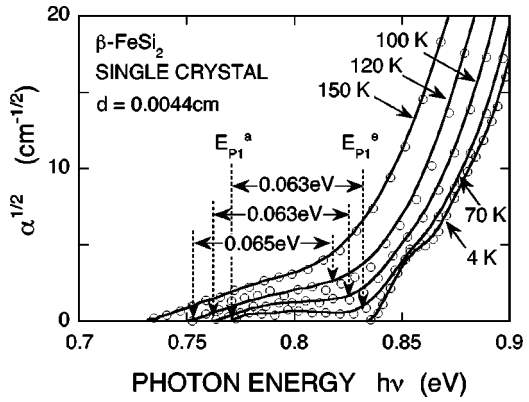

FIG. 1. The low-level absorption spectra near the absorption edge of single crystalline β-$FeSi_2$ at various temperatures.

[a]Author to whom correspondence should be addressed; electronic mail: udono@ee.ibaraki.ac.jp

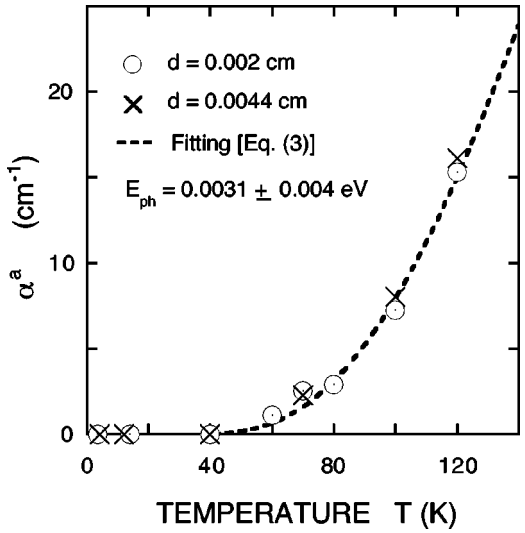

FIG. 2. Temperature dependence of the strength of absorption component α^a. The phonon energy $E_{ph}=0.031\pm0.004$ eV was obtained from the fitting to Eq. (3).

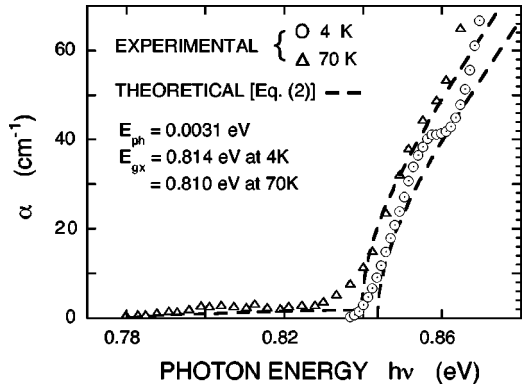

FIG. 3. The edge-absorption spectra of β-$FeSi_2$ at 4 and 70 K. The components associated with the phonon emission and absorption compared with the theoretical expression of Eq. (2), with the assumption of the one phonon energy of 0.031 eV.

superscripts denote whether the phonon is emitted (e) or absorbed (a) during the optical absorption process. The strength of the phonon absorbed component with threshold at E_{P1}^e decreased with decreasing the temperature, and the component was not present below about 40 K. The difference between E_{P1}^e and E_{P1}^a was the same for each temperature within experimental uncertainty. Thus, E_{P1}^e and E_{P1}^a would be related to the thresholds of indirect transitions with a phonon emission or absorption. From the observation of several absorption spectra in different samples, we found only one dominant phonon structure. Therefore, we analyze the spectra using one dominant phonon of energy E_{ph}.

We will assume that the Coulomb interaction between the excited electrons and holes is strong enough for the creation of free excitons to play a significant role in the optical absorption spectrum at the low temperature, as is so for Ge, Si, and GaP.[19–21] Then, the optical absorption of indirect allowed transitions should be of the form[22]

$$\alpha(h\upsilon)=\frac{A}{\exp(E_{ph}/kT)-1}(h\upsilon-E_{gx}+E_{ph})^{1/2}+\frac{B\exp(E_{ph}/kT)}{\exp(E_{ph}/kT)-1}(h\upsilon-E_{gx}-E_{ph})^{1/2}, \quad (2)$$

for the pair of component associated with a given phonon of energy E_{ph}, which has the momentum required to take the electron from the valence-band maxima to the conduction-band minima. The energy E_{gx} is just the band-gap energy minus an exciton binding energy.The quantities A and B are parameters containing the density-of-state effective masses of electrons and holes. k is Boltzmann's constant. According to Eq. (2), the strength of the absorption component α^a is proportional to the available phonon, and the strength depended on the temperature is given by

$$\alpha^a(T)\propto\frac{A}{\exp(E_{ph}/kT)-1}. \quad (3)$$

Figure 2 shows the temperature dependence of absorption coefficient at the energy thresholds E_{P1}^e for each spectra. The absorption coefficient at the energy thresholds increased with increasing the temperature as followed in Eq. (3). Thus, we obtained a phonon energy $E_{ph}=0.031\pm0.004$ eV from the fitting curve using Eq. (3). Excellent agreement between the experimental absorption coefficient and the theoretical fitting provides convincing evidence that the absorption band comes from the phonon-assisted transition to the exciton state. Tassis *et al.* and Lange *et al.* reported the phonon band at 268.2 and 261 cm^{-1}, respectively, by infrared (IR) absorption measurements on β-$FeSi_2$ films on Si.[7–13] Guzzeti *et al.* pointed out that the highest-intensity peak was at about 250 cm^{-1} for the Raman spectra measured on single crystalline β-$FeSi_2$.[23] Our phonon energy agreed with those reported values. Different weak phonon peaks were also reported in the IR and Raman spectra. However, the phonon energy dominantly determining absorption profiles is believed to be 0.031 eV.

We compared the experimental absorption spectra as the basic shape to the theoretical temperature dependence, on the assumption that the phonon energy of 0.031 eV is dominant during the optical transition in our crystals. The results of such a comparison for 4 and 70 K were shown in Fig. 3. So by considering only one phonon energy, rather good agreement between the experimental spectra and the calculated spectra is obtained. In our experiment, the ratio B/A of the best-fitted spectra is not just unity but around 3.3. From the fitting of the spectra, we obtained $E_{gx}=0.814$ eV at 4 K and $E_{gx}=0.810$ eV at 70 K. These values are approximately 0.1 eV lower than the values of the reported direct energy gap that were measured from β-$FeSi_2$ films on Si.[7–11] Based on the phonon-assisted transition probabilities, the small energy difference $\delta E=0.1$ eV and the phonon energy $E_{ph}=0.031$ eV can gave the ratio $B/A=(\delta E+E_{ph})^2/(\delta E-E_{ph})^2=3.6$, which is close to the experimental B/A. This agreement gives us the following definitive conclusion, β-$FeSi_2$ is an indirect band-gap semiconductor, although the direct gap is very close to the indirect one.

In conclusion, we have measured the optical absorption spectra near the fundamental absorption edge of β-$FeSi_2$ single crystals by transmission measurements. The stepped structure corresponding to the phonon emission and absorption is observed in the low-temperature absorption spectra below about 150 K. We determined the exciton transition energy E_{gx} is about 0.814 eV at 4 K and about 0.810 eV at 70 K, and also obtained a phonon energy $E_{ph}=0.031\pm0.004$ eV from the analysis of the spectra. Our ex-

perimental results reveal that β-$FeSi_2$ has an indirect band gap.

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