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Indirect optical absorption of single crystalline $\beta$-FeSi$_2$

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We investigated optical absorption spectra near the fundamental absorption edge of $\beta$-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]

$\beta$-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 $\mu$m by introducing $\beta$-FeSi$_2$ particles into a silicon bipolar junction.$^{3,4}$ Chu et al. also demonstrated the 1.57 $\mu$m electroluminescence (EL) at room temperature from sputter-deposited $\beta$-FeSi$_2$ films on Si.$^5$ However, the luminescence mechanism in $\beta$-FeSi$_2$ is not clearly understood, because the electronic structure of $\beta$-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 $\beta$-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 $\beta$-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 gap, respectively.$^{13–15}$ The 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 $\beta$-FeSi$_2$ single crystals. In this letter, we report optical transmission measurements of $\beta$-FeSi$_2$ single crystals.

Single crystalline $\beta$-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 $1.5 \times 10^{19}$ cm$^{-3}$ at 300 K and less than $1 \times 10^{16}$ 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 a double-beam spectrophotometer (Hitachi U-4000). Reflection measurements were made at 300 K using a UV-VIS-NIR microspectrophotometer (Nippon Bunko). The absorption coefficient $\alpha$ was obtained by solving the following equation, assuming that the temperature dependence of reflectivity $R$ was negligible throughout the measured spectra region (0.7–1.0 eV):

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

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 $hv$ 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 $E_{P1}^a$ and $E_{P1}^b$ 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 $\beta$-FeSi$_2$ at various temperatures.
FIG. 2. Temperature dependence of the strength of absorption component $a'$. The phonon energy $E_{ph} = 0.031 \pm 0.004$ eV was obtained from the fitting to Eq. (3).

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 $a'$ is proportional to the available phonon, and the strength depended on the temperature is given by

$$a'(T) \propto \frac{A}{\exp(E_{ph}/kT) - 1}.$$  

Figure 2 shows the temperature dependence of absorption coefficient at the energy thresholds $E_{P1}^{s}$ 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 $E_{ph} = 0.031 \pm 0.004$ 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 $\beta$-FeSi$\textsubscript{2}$ films on Si. Guzzetti et al. pointed out that the highest-intensity peak was at about 250 cm$^{-1}$ for the Raman spectra measured on single-crystalline $\beta$-FeSi$\textsubscript{2}$. 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 $\beta$-FeSi$\textsubscript{2}$ films on Si. 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, $\beta$-FeSi$\textsubscript{2}$ 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 $\beta$-FeSi$\textsubscript{2}$ 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 $E_{ph} = 0.031 \pm 0.004$ eV from the analysis of the spectra. Our experimental absorption spectra have the same basic shape to the theoretical expression of Eq. (2), with the assumption of the one phonon energy of 0.031 eV.
experimental results reveal that $\beta$-FeSi$_2$ has an indirect band gap.

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