Evaluation of minority-carrier diffusion length in n-type beta-FeSi2 single crystals by electron-beam-induced current

Evaluation of minority-carrier diffusion length in *n*-type *β*-FeSi₂ single crystals by electron-beam-induced current

Teruhisa Ootsuka[a)] and Takashi Suemasu
Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Jun Chen and Takashi Sekiguchi
Advanced Electronic Materials Center, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

We have evaluated the diffusion length of minority carriers (holes) in single-crystalline *n*-type β-FeSi₂ bulk grown by chemical vapor transport by means of electron-beam-induced current (EBIC) technique in the edge-scan configuration. The EBIC line-scan data showed a clear exponential dependence of distance from the Al electrode. The diffusion length was estimated to be 20 μm at room temperature, and increased upon high-temperature annealing, reaching approximately 30 μm after annealing at 800 °C for 8 h. This result explained the improvement of photoresponsivity in the Al/*n*-β-FeSi₂ Schottky diodes by high-temperature annealing. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2835904]

Semiconducting iron disilicide (β-FeSi₂) has a band gap of approximately 0.78 eV,[1] and a very large optical absorption coefficient of over 10^5 cm⁻¹ at 1 eV.[2] Thus, β-FeSi₂ has been attracting attention recently as a material for Si-based optoelectronic devices operating at wavelengths used for optical fiber communication. β-FeSi₂ is also considered to be an environmentally friendly semiconductor since both Si and Fe are nontoxic and occur abundantly in the earth's crust. Over the several years, there have been numerous attractive reports on the light-emitting diodes using β-FeSi₂.[3–9] In contrast, there have been a limited number of reports on photodetectors using β-FeSi₂.[10–14] In particular, there have been only a few reports so far discussing the photoresponsivity of β-FeSi₂. The highest photoresponsivity ever is approximately 0.1 mA/W at 1.60 μm.[12] This small photoresponsivity is considered be due to defects at the grain boundaries of β-FeSi₂ films. Most photoresponse experiments on β-FeSi₂ have so far involved β-FeSi₂/Si heterostructures using β-FeSi₂ continuous films formed on Si since β-FeSi₂ can be grown epitaxially on Si substrates. However, due to the small difference between the constants *b* and *c* of β-FeSi₂, β-FeSi₂ tends to form a few kinds of epitaxial variants on both Si(001) and Si(111).[15] Thus, the β-FeSi₂ grain size is not large enough compared to the spot size of the light used in optical measurements. Furthermore, we cannot rule out the photoexcited carriers originating from Fe-related deep levels in Si in the case of β-FeSi₂ film/Si,[12–14] making it difficult to understand the intrinsic photoresponse properties of β-FeSi₂. One way to avoid these problems is to measure the photoresponsivity in β-FeSi₂ single crystals. In our previous paper, we have fabricated an Al/*n*-β-FeSi₂ Schottky diode structure using β-FeSi₂ single crystals grown by chemical vapor transport (CVT), and reported an enhanced photoresponsivity in β-FeSi₂.[16] The photoresponsivity reached 22 mA/W at 1.31 μm for as-grown sample, and increased up to 58 mA/W upon annealing at 800 °C for 8 h. These values are more than two orders of magnitude larger than the highest value ever reported. However, the mechanism of this improvement in photoresponsivity has not yet been made clear. Electron-beam-induced current (EBIC) technique is considered to be one of the most powerful methods for investigating the electrical studies of various semiconductor materials.[17] In this letter, we have evaluated a minority-carrier diffusion length of β-FeSi₂ single crystals for the first time using a simple Al/*n*-β-FeSi₂ Schottky diode by EBIC technique. The obtained diffusion length was unexpectedly very large, being approximately as large as 20–30 μm. The effect of high-temperature annealing on photoresponsivity and diffusion length was also discussed.

An Al/*n*-type β-FeSi₂ Schottky junction was formed as follows. First, β-FeSi₂ single crystals were grown by the CVT method using I₂ as a transport agent. β-FeSi₂ used in this study showed *n*-type conductivity. The detailed procedure was described in our previous paper.[16] Then, the grown-up crystals were annealed at 800 °C for 8 h in vacuum ($<2 \times 10^{-4}$ Pa), and they were dipped in a 5% HF solution for more than 2 min to remove the surface damaged layers. The front surface contact was formed with 1 wt % Si Al wires by the ultrasonic wedge bonding machine, and the back surface contact was formed with In solder. The photoresponse properties were measured at RT using a white halogen lamp and a single monochromator. The light intensity was calibrated by Hamamatsu photodiodes S2281-21 and P8079-21. The EBIC observation was done in the edge-scan configuration with a Hitachi S4200 field-emission scanning electron microscope in EBIC mode at RT.[18,19] The acceleration voltage of electron beam V_{ac}, was varied from 7.5 to 25 kV.

Figure 1 shows a typical example of photoresponse spectra measured at RT for as-grown and annealed samples. The photocurrent is observed for photon energies greater than approximately 0.8 eV and increases sharply with increasing photon energy for both samples. The interpretation of the spectra was given in our previous paper.[16] The photoresponsivity was enhanced for the annealed sample. Similar results were obtained for other samples. In brief, the photoresponsivity was enhanced for samples annealed at temperatures such as 800 and 850 °C, higher than the temperature of the

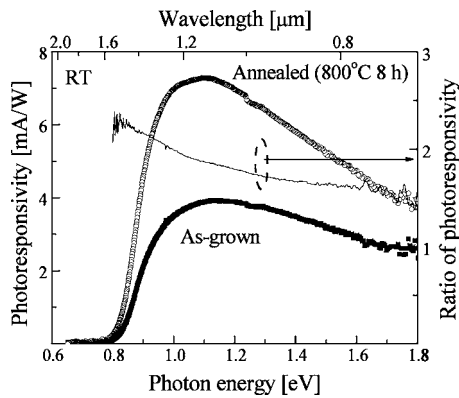a)Electronic mail: bk200730352@s.bk.tsukuba.ac.jp.

FIG. 1. Spectral response of as-grown and annealed samples measured at RT. The improved ratio in photoresponsivity for annealed sample relative to that for as-grown one is also shown.

crystallization zone in the CVT method (750–780 °C).[16] On the other hand, the photoresponsivity was not enhanced for samples annealed at temperatures lower than the above crystallization temperature. This result shows that the annealing that exceeds the crystallization temperature is indispensable for enhancing the photoresponsivity of β-FeSi$_2$. The improved ratio in photoresponsivity for the annealed sample relative to that for the as-grown one is also shown. The photoresponsivity was improved, in particular, for longer-wavelength regions, as shown in Fig. 1. This result suggests that the photons with lower energies penetrated deeper into the β-FeSi$_2$ crystal, and more carriers were generated and collected. In order to investigate what happened in the β-FeSi$_2$, we performed EBIC observations.

Figures 2(a) and 2(b) show EBIC and secondary-electron (SE) images around the Al contact, respectively, with $V_{ac} = 10$ kV. In the EBIC method, the carriers generated within a diffusion length on the n-type β-FeSi$_2$ are collected by the electric field under the Al contact and sensed as a
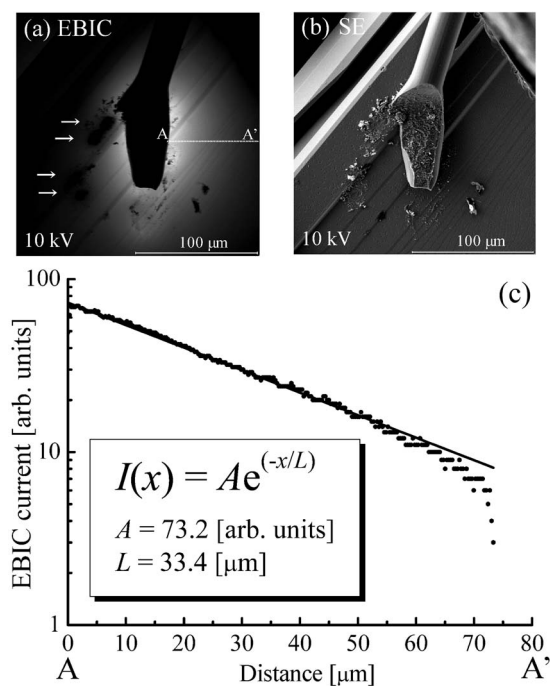

FIG. 2. (a) EBIC and (b) SE images around the Al contact. (c) is the semilogarithmic plot of EBIC line-scan profile along the line from points A to A'.
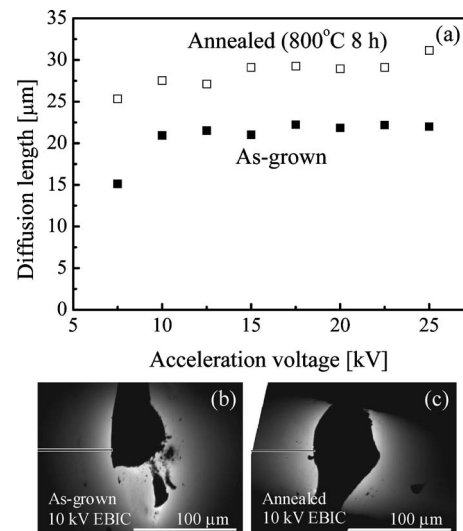

FIG. 3. (a) Dependence of diffusion length on V_{ac} obtained for as-grown (■) and annealed samples (□). (b) and (c) show the EBIC images of as-grown and annealed samples.

current in the external circuit. In Fig. 2(a), the brighter regions indicate higher collection of electron-beam-induced carriers in the β-FeSi$_2$. On the other hand, the dark spots pointed by white arrows show surface damaged regions caused probably by a bonding wedge. Figure 2(c) shows the semilogarithmic plot of EBIC line-scan data along the line AA' for the annealed sample. The EBIC profile shows a clear exponential dependence of distance from the Al contact. Several theoretical models have been used to extract the diffusion length by fitting the theoretical expression to the EBIC line-scan data. In this work, the diffusion length was roughly estimated to be 33 μm, assuming that the EBIC profile varies as $\exp(-x/L)$, where x is the distance from the Al edge (point A) along the line, and L the diffusion length of holes, that is, electron-beam-induced minority carriers in the n-type β-FeSi$_2$.

Figure 3(a) shows the dependence of diffusion length on V_{ac} for other as-grown and annealed samples. The EBIC images for these samples are shown in Figs. 3(b) and 3(c), respectively. The diffusion length is less dependent on V_{ac} for both as-grown (■) and annealed samples (□) for $V_{ac} > 10$ kV. We therefore speculate that the penetration depth is much smaller than the diffusion length. The penetration depth of the electron beam is estimated to be 1 μm at $V_{ac} = 10$ kV from the density of β-FeSi$_2$ (4.93 g/cm^3),[20] showing that our assumption is valid. The penetration depth at $V_{ac} = 7.5$ kV is approximately 0.5 μm. Thus, the decrease in diffusion length at $V_{ac} = 7.5$ kV for both samples is considered to be due to surface recombination of carriers. The diffusion length of the annealed sample (□) reaches approximately 30 μm at $V_{ac} = 10$ kV. This value is almost the same as that for the annealed sample shown in Fig. 2. The shape of the Al contact on the β-FeSi$_2$ is likely to affect the EBIC images; however, the diffusion length for the annealed sample is always larger than that for as-grown sample. On the basis of these results, we conclude that the higher photoresponsivity in the annealed sample, shown in Fig. 1, is attributed to the enhanced diffusion length of holes. We think that the enhancement of diffusion length in β-FeSi$_2$ by high-temperature annealing is attributed to improvement of carrier lifetime. Even in the preliminary experimental results, it was

found that the carrier lifetime obtained from the transient behavior in photoconductivity of β-FeSi$_2$ bulk crystals when excited by 1.31 μm light pulse was increased after high-temperature annealing. At present, we cannot discuss values of carrier lifetime themselves because they are easily influenced by configuration of electrodes, and thus we have to pay more attention when dealing with them. However, we can say at least that even the annealing performed at temperatures higher only by 20–50 °C than the crystallization temperature of the CVT method improves the crystallinity of β-FeSi$_2$.

In conclusion, we have fabricated Al/n-β-FeSi$_2$ Schottky diode structures using single-crystalline n-type β-FeSi$_2$ by CVT, and investigated the diffusion length of hole by means of EBIC technique. The photoresponsivity of the diode was improved after high-temperature annealing. The diffusion length was increased from approximately 20 to 30 μm at RT after annealing at 800 °C for 8 h in vacuum.

[1] H. Udono, I. Kikuma, T. Okuno, Y. Masumoto, and H. Tajima, Appl. Phys. Lett. **85**, 1937 (2004).
[2] M. C. Bost and J. E. Mahan, J. Appl. Phys. **58**, 2696 (1985).
[3] D. Leong, M. Harry, K. J. Reeson, and K. P. Homewood, Nature (London) **387**, 686 (1997).
[4] T. Suemasu, Y. Negishi, K. Takakura, and F. Hasegawa, Jpn. J. Appl. Phys., Part 2 **39**, L1013 (2000).
[5] T. Suemasu, Y. Negishi, K. Takakura, and F. Hasegawa, Appl. Phys. Lett. **79**, 1804 (2001).
[6] S. Chu, T. Hirohada, M. Kuwabara, H. Kan, and T. Hiruma, Jpn. J. Appl. Phys., Part 2 **43**, L127 (2004).
[7] M. Takauji, C. Li, T. Suemasu, and F. Hasegawa, Jpn. J. Appl. Phys., Part 1 **44**, 2483 (2005).
[8] S. Murase, T. Sunohara, and T. Suemasu, J. Cryst. Growth **301-302**, 676 (2007).
[9] T. Suemasu, Y. Ugajin, S. Murase, T. Sunohara, and M. Suzuno, J. Appl. Phys. **101**, 124506 (2007).
[10] K. Lefki and P. Muret, J. Appl. Phys. **74**, 1138 (1993).
[11] Y. Maeda, K. Umezawa, Y. Hayashi, K. Miyake, and K. Ohashi, Thin Solid Films **381**, 256 (2001).
[12] Z. X. Liu, M. Osamura, T. Ootsuka, S. Wang, Y. Fukuzawa, Y. Suzuki, R. Kuroda, T. Mise, N. Otogawa, Y. Nakayama, H. Tanoue, and Y. Makita, Opt. Mater. (Amsterdam, Neth.) **27**, 942 (2005).
[13] Y. Makita, T. Ootsuka, Y. Fukuzawa, N. Otogawa, H. Abe, Z. X. Liu, and Y. Nakayama, Proc. SPIE **6197**, 619700 (2006).
[14] M. Shaban, K. Nakashima, W. Yokoyama, and T. Yoshitake, Jpn. J. Appl. Phys., Part 2 **46**, L667 (2007).
[15] J. E. Mahan, V. Le Thanh, J. Chevrier, I. Berbezier, J. Derrien, and R. G. Long, J. Appl. Phys. **74**, 1747 (1993).
[16] T. Ootsuka, Y. Fudamoto, M. Osamura, T. Suemasu, Y. Makita, Y. Nakayama, and Y. Fukuzawa, Appl. Phys. Lett. **91**, 142114 (2007).
[17] H. J. Leamy, J. Appl. Phys. **53**, R51 (1982).
[18] J. Chen, T. Sekiguchi, D. Yang, F. Yin, K. Kido, and S. Tsurekawa, J. Appl. Phys. **96**, 5490 (2004).
[19] J. Chen, T. Sekiguchi, N. Fukata, M. Takase, T. Chikyow, K. Yamabe, R. Hasunuma, Y. Akasaka, S. Inumiya, Y. Nara, and Y. Yamada, Appl. Phys. Lett. **89**, 222104 (2006).
[20] K. Kanaya and S. Okayama, J. Phys. B **5**, 43 (1972).