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Photoresponse properties of Al/n-β-$FeSi_2$ Schottky diodes using β-$FeSi_2$ single crystals

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We have clearly observed photoresponse properties in an Al/n-β-$FeSi_2$ structure using β-$FeSi_2$ single crystals grown by chemical vapor transport. A photocurrent is observed for photons with energies greater than 0.68 eV. It increases sharply with increasing photon energy and attains a maximum at approximately 0.95 eV (1.31 μm). The photocurrent originated from the photoexcited electrons in the Al and the band-to-band photoexcited carriers in the β-$FeSi_2$ located under the Al contact. The photoresponsivity increased upon high-temperature annealing, reaching 58 mA/W at 0.95 eV after annealing at 800 °C for 8 h. © *2007 American Institute of Physics*.
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β-$FeSi_2$ has been attracting attention recently as a material for Si-based light emitters and detectors operating at wavelengths used for optical fiber communication.[1] This is because β-$FeSi_2$ has a band gap of approximately 0.78 eV,[2] and a very large optical absorption coefficient of over 10^5 cm^{-1} at 1 eV.[1] β-$FeSi_2$ 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 last decade, there have been numerous reports on light-emitting diodes using β-$FeSi_2$.[3–8] In contrast, there have been a limited number of reports on photodetectors of β-$FeSi_2$.[9–13] In particular, there have been only a few reports so far discussing the photoresponsivity of β-$FeSi_2$.[11] We think that this is because photoresponsivity requires high-quality β-$FeSi_2$ with a certain area since photogenerated carriers must be collected efficiently. Most photoresponse experiments on β-$FeSi_2$ have so far involved β-$FeSi_2$/Si heterostructures using β-$FeSi_2$ continuous films formed on Si since β-$FeSi_2$ can be grown epitaxially on Si substrates.[14] However, the β-$FeSi_2$ grain size is not large enough compared to the spot size of the light used in optical measurements. This is because it is difficult to fabricate single-crystalline β-$FeSi_2$ films on Si substrates. Due to the small difference between the lattice constants b and c of β-$FeSi_2$, β-$FeSi_2$ tends to form a few kinds of epitaxial variants on both Si(001) and Si(111).[14] Furthermore, we cannot rule out the photoexcited carriers originating from Fe-related deep levels in Si in the case of β-$FeSi_2$ film/Si,[13,15,16] making it difficult to understand the photoresponse properties. Thus, it is meaningful to measure the photoresponsivity in single-crystalline β-$FeSi_2$ bulk crystals in order to obtain the intrinsic photoresponse properties of β-$FeSi_2$. In this paper, we have fabricated a simple Al/n-β-$FeSi_2$ structure using β-$FeSi_2$ single crystals prepared by the chemical vapor transport (CVT) method. The photoresponsivity of the device was measured and the effect of high-temperature annealing on photoresponsivity was discussed.

β-$FeSi_2$ single crystals were grown by the CVT method using I_2 as a transporting agent and powdered 5N Fe and 4N up Si as source material. The starting material was enclosed in a quartz ampoule. The ampoule was evacuated and inserted into a two-zone furnace. The temperatures in the dissolution zone and the crystallization zone were maintained at

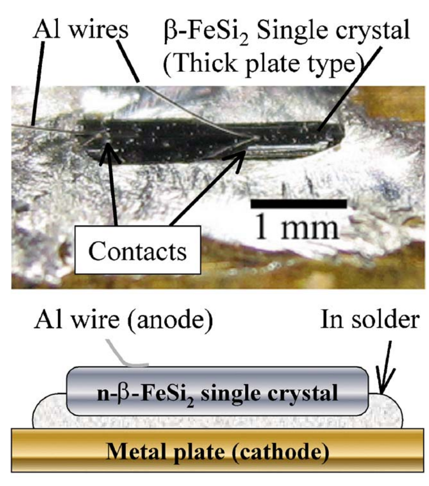

FIG. 1. (Color online) Typical photograph of Al/β-$FeSi_2$ and a schematic cross section of the device. This device has two Al wires connected to the front surface of β-$FeSi_2$. The back surface contact was formed with In solder.

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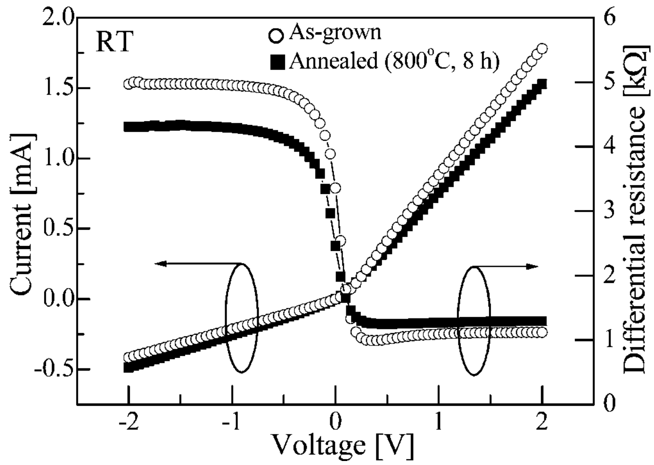

FIG. 2. The current-voltage characteristics of as-grown and annealed samples measured at room temperature. The differential resistances of the samples are shown as well.

1000 and 750 °C, respectively, for two weeks. After the samples were removed, high-temperature annealing was performed at 800 °C for 8 h in vacuum ($<2\times10^{-4}$ Pa). The samples were immersed in an HF (5%) solution at room temperature for approximately 2 min to cleanse the surface. Next, the front surface contact was formed with 1 wt % Si Al wires by an ultrasonic wedge bonding machine, and the back surface contact was formed with an In solder, as shown in Fig. 1. Two Al bonding wires were connected to the β-$FeSi_2$ in order to check the reproducibility of measured properties. In general, CVT yields needle-type β-$FeSi_2$ crystals. However, it also produces a certain number of platelike β-$FeSi_2$ crystals.[17] In the present study, we chose to use thick platelike β-$FeSi_2$ crystals because a large photoresponsivity could not be obtained on thin platelike crystals. The photoresponse properties were measured using a white halogen lamp and a

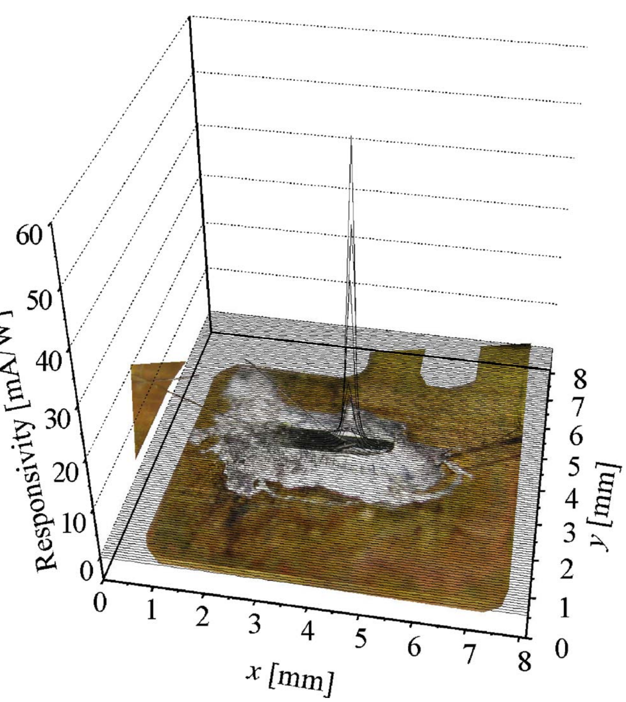

FIG. 3. (Color online) Mapping of photoresponsivity under laser illumination. The wavelength and the output power of the laser were 1.31 μm and 1.0 mW, respectively. The spot size was approximately 50 μm.

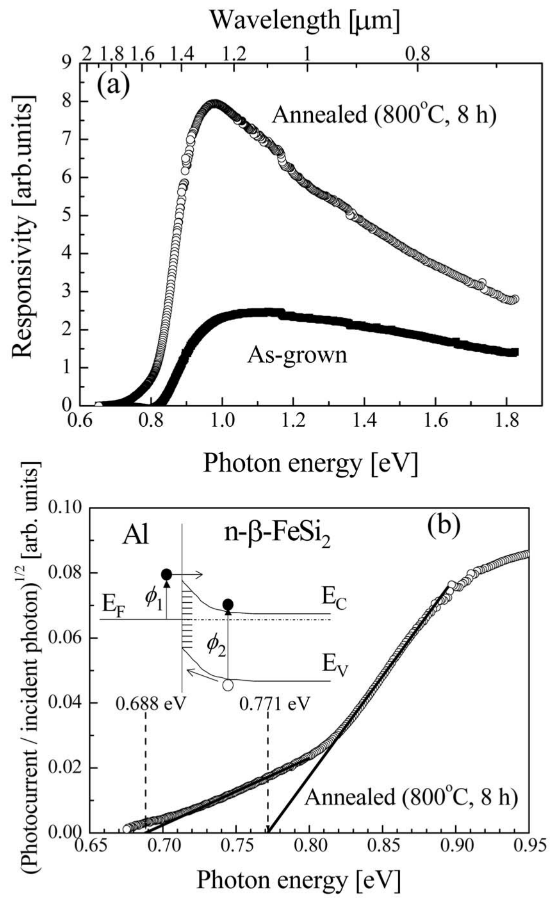

FIG. 4. (a) Spectral response of as-grown and annealed samples, and (b) square root of the photocurrent per incident photon vs photon energy for the annealed sample.

single monochromator (JASCO MCA-50HP) with a focal length of 500 mm. The light intensity was calibrated by Hamamatsu photodiodes S2281-21 and P8079-21. The in-plane distribution of the photoresponsivity was measured by scanning a 1 mW semiconductor laser light with a wavelength of 1.31 μm. The spot size of the laser light was approximately 50 μm.

The platelike β-$FeSi_2$ used in this study showed n-type conductivity in the Hall measurements using the van der Pauw method. Details of the electrical properties of the β-$FeSi_2$ itself will be reported elsewhere. The current-voltage characteristics of the sample are shown in Fig. 2. Rectifying properties can be clearly observed. More current flows when a positive bias is applied to the Al wire with respect to the In solder. These results indicate that the Al/n-type β-$FeSi_2$ junction forms a Schottky diode even though there is a large series resistance and leakage currents. The series and parallel resistances of the device were estimated to be approximately 1 and 3 kΩ, respectively, for both samples.

Under illumination, the positive voltage appeared on the Al wire with respect to the In solder. Figure 3 shows the in-plane distribution of photoresponsivity under illumination by a 1.31 μm laser. The photoresponsivity reached a maximum at this wavelength, as shown later. The photoresponse was observed only around the Al wire. These results indicate that the electrons and holes generated in the depletion region of β-$FeSi_2$ under the Al or holes generated in the n-type β-$FeSi_2$ within a diffusion length of it are collected by the electric filed, leading to a current in the external circuit. The highest photoresponsivity was 22 mA/W for the as-grown sample and 58 mA/W for the annealed sample. These values are more than two orders of magnitude higher than the highest values ever reported.[11] Even in the preliminary results, the value of 58 mA/W corresponds to a quantum efficiency of 5.5% for a wavelength of 1.31 μm.

Figure 4(a) shows the photoresponse spectra for as-grown and annealed samples. The photocurrent is observed for photon energies of approximately 0.8 eV and increases sharply with increasing photon energy for both samples. The photoresponse was greatly enhanced for the annealed sample, suggesting that high-temperature annealing is very effective in improving the crystallinity of β-$FeSi_2$. In order to investigate in detail the photoresponse properties of the annealed sample, we plotted the square root of the photocurrent per incident photon against photon energy $h\nu$ as shown in Fig. 4(b). Two straight lines were obtained. The two extrapolated values on the energy axis, ϕ_1 and ϕ_2, are approximately 0.69 and 0.77 eV. The photocurrent shows a gradual increase for 0.69 eV $< h\nu <$ 0.77 eV, followed by a sharp increase for $h\nu >$ 0.77 eV. Thus, the values of ϕ_1 and ϕ_2 are thought to give the barrier height at the Al/n-β-$FeSi_2$ junction and the band gap of β-$FeSi_2$, respectively. The value of ϕ_1 differed to some extent from sample to sample, while ϕ_2 was always fixed at 0.76±0.01 eV. In addition, it is almost the same as the value reported as the indirect absorption edge in Ref. 2. Thus, we can say that the photoresponse spectrum in Fig. 4(b) accounts for the photocurrents due to electrons photoexcited in the Al surmounting the barrier height for smaller photon energies, and due to electrons and holes photoexcited in the β-$FeSi_2$ for larger photon energies.

In summary, we have fabricated an Al/n-β-$FeSi_2$ structure using β-$FeSi_2$ single crystals grown by CVT, and clearly observed photoresponse properties for photons with energies greater than 0.68 eV. The photoresponse reached a maximum at approximately 0.91 eV (1.31 μm). The photoresponsivity increased from 22 to 58 mA/W at 0.91 eV after annealing at 800 °C for 8 h.

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