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Growth of p-type β-$FeSi_2$ polycrystalline films by RF magnetron sputtering

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β-$FeSi_2$ polycrystalline films with p-type conduction were grown by RF magnetron sputtering using a B-doped p^+-Si target with Fe chips. The hole density and mobility were 2×10^{17} cm^{-3} and 71 $cm^2V^{-1}s^{-1}$ at RT, respectively. The acceptor levels formed by the B-doping were obtained to be 10 and 245 meV. In the temperature dependence of electrical properties, the p-type β-$FeSi_2$ film showed the impurity-band conduction at 77−350 K.

1. Introduction

β-$FeSi_2$ thin films on Si substrate are one of the candidates for silicon-based photovoltaic (PV) applications with a theoretical conversion efficiency of 16−23% [1,2]. A large optical absorption coefficient of over 10^5 cm^{-1} at 1.0 eV indicates a fabrication of thin film β-$FeSi_2$ solar cells which imply low material consumption of abundant and eco-friendly elements [3,4]. Although the attractive PV properties of β-$FeSi_2$, a low conversion efficiency less than 1% has been reported in β-$FeSi_2$ polycrystalline solar cells [5,6]. These β-$FeSi_2$ polycrystalline thin films grown by RF magnetron sputtering generally showed high density of residual carrier (p, n > $10^{18\text{-}20}$ cm^{-3}) and low carrier mobility (6−250 $cm^2V^{-1}s^{-1}$). Recently, we have succeeded in the growth of undoped β-$FeSi_2$ polycrystalline films with a low electron density (2×10^{16} cm^{-3}) and a high mobility (~800 $cm^2V^{-1}s^{-1}$) by RF magnetron sputtering [7]. The n-type conduction of the undoped β-$FeSi_2$ polycrystalline films was found to originate from unintentionally-doped As included in Fe source. For an application to the photovoltaic devices, it is necessary to control the conduction type and the carrier density by the same growth method. In this study, boron was doped in the β-$FeSi_2$ polycrystalline films by the same growth procedure to obtain p-type conduction. The electrical properties of the obtained p-type films were measured to investigate an acceptor level formed by the B-doping. In the temperature dependence of the electrical properties, the conduction mechanism was also investigated to compare with that in the undoped films.

2. Experiments

The B-doped samples were grown by RF magnetron sputtering. The p^+-type Si wafer attached with high-purity Fe chips (Toho Zinc Mairon UHP, 5N) was used as the sputtering target for the co-deposition of Fe, Si and B. The B-concentrations in the p^+-type Si was 10^{19}–10^{20} cm^{-3}. The number of Fe chips was determined as the composition ratio became Si/Fe ≈ 2.0 in the deposited films by X-ray fluorescence (XRF) measurements. The base pressure of the growth chamber was 1×10^{-4} Pa and the growth pressure was 1 Pa with an Ar flow rate of 4 sccm. The RF power for sputtering was fixed

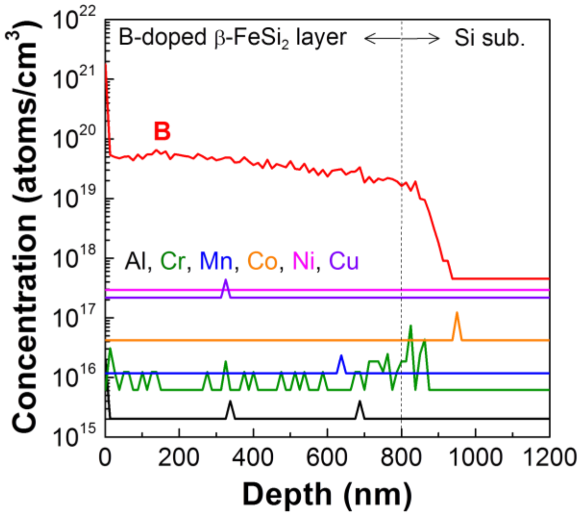

Fig. 1 SIMS depth profiles of impurities in 800-nm-thick β-$FeSi_2$ film annealed for 32 h.

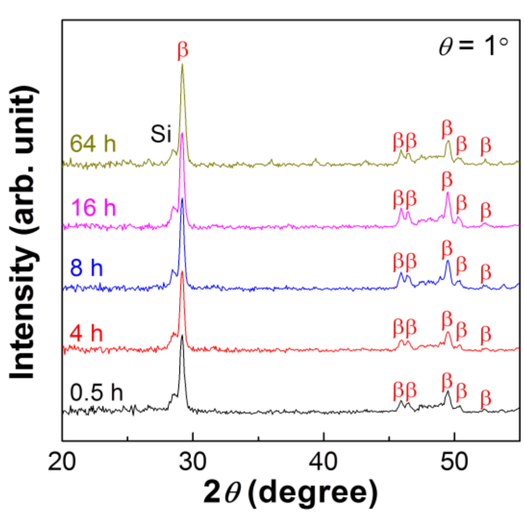

Fig. 2 XRD patterns of β-$FeSi_2$ films annealed at different times.

at 50 W (13.56 MHz). The B-doped Fe-Si amorphous layers of 200−800 nm thickness were deposited on FZ n-Si substrates with a thickness of 550 μm at room temperature (RT). The resistivity of the Si substrate was higher than 1 kΩ·cm. The amorphous layers were cut into pieces and annealed at 800 °C for silicidation reaction in a rapid thermal annealing (RTA) furnace. In the annealing processes, the initial rate of temperature increase to 800 °C (T_r) was fixed at T_r = 1 min and the annealing time at 800 °C (T_a) was changed in T_a = 0.5−64 h. In the SIMS measurements, the depth profiles of impurity elements were measured using the primary ions O_2^+ and Cs^+ in the film of 800 nm thickness. All the impurities included in the 5N Fe source (B, Al, Cr, Mn, Co, Ni, Cu, Pb, P, S, and As) were analyzed using the two primary ion beams. Crystalline structures and electrical properties were measured in the film with 200 nm thickness. The crystalline structures were evaluated by 2θ scan at θ = 1° in X-ray diffraction (XRD) measurements. In the electrical measurements, ohmic contacts of Al electrodes were formed on the films after removing the native oxide layer. The resistivity (ρ), carrier density (n), and mobility (μ) were measured at temperatures between 80 and 370 K using the van der Pauw method.

3. Results and Discussion

Figure 1 shows the SIMS depth profiles of representative impurities in the B-doped β-$FeSi_2$ film annealed for 32 h. The averaged B concentration in the β-$FeSi_2$ layer was about 4 × 10^{19} cm^{-3}. The B-concentration in the film was almost the same as that in the p^+-Si target wafer. The concentrations of other impurities (B, Al, Cr, Mn, Co, Ni, Cu, Pb, P, and S) were lower than the detection limit. In the undoped film, the main impurity was As of 2–5×10^{18} cm^{-3} (not shown). The As was unintentionally doped from the 5N Fe source. Therefore, it is expected that the B-doped films include the same amount of As. The XRD patterns of the annealed films are shown in Fig. 2. In this figure, the XRD peaks of β-$FeSi_2$ is marked β. As seen in the figure, all the films showed the formation of β-$FeSi_2$ single phase without other phases of α-Fe_2Si_5, γ-$FeSi_2$ and ε-FeSi. The annealing-time dependence of the carrier density is plotted in Fig. 3. The film annealed for 0.5 h showed n-type conduction with the electron density of 9×10^{16} cm^{-3}. While, the films annealed for T_a = 8–16 h showed p-type conduction with the hall density of ~2 × 10^{17} cm^{-3} and the hole mobility of ~71 $cm^2V^{-1}s^{-1}$. So, it was found that the B-doped β-$FeSi_2$ polycrystalline films showed p-type conduction after the long-

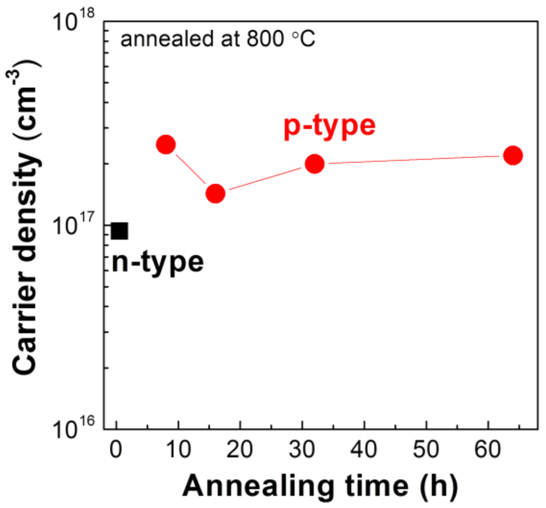

Fig. 3 Carrier density as a function of annealing time.

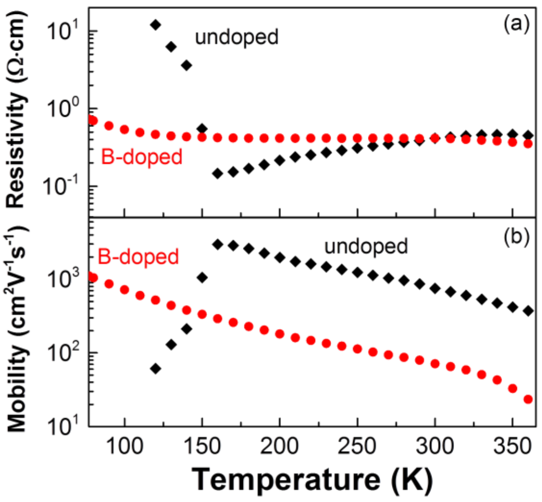

Fig. 4 Temperature dependences of (a) resistivity and (b) mobility in β-$FeSi_2$ polycrystalline films.

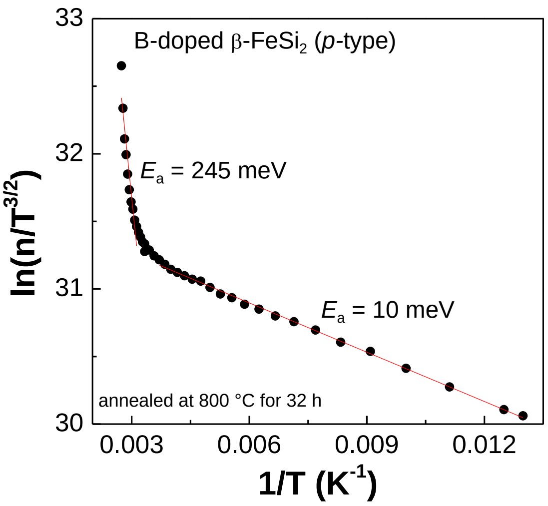

Fig. 5 Temperature dependence of hole density in B-doped β-$FeSi_2$ film annealed for 32 h.

time annealing. Figure 4 shows the temperature dependences of (a) resistivity and (b) mobility in the p-type β-$FeSi_2$ polycrystalline film annealed for 32 h. For comparison, the result in the undoped β-$FeSi_2$ polycrystalline film is also shown in the figure. In the undoped films, the resistivity increased and the mobility decreased rapidly at lower temperature than 160 K. The result shows that the conduction mechanism is changed at the transition temperature (T_T). The band conduction at $T > T_T$ and the localized conduction at $T < T_T$ are dominant conduction mechanisms, respectively [7-9]. While, in the B-doped film, the resistivity and the mobility were increased as temperature decreases, but the T_T was not observed. The temperature dependence of hole density in the B-doped film is shown in Fig. 5. As shown in the figure, two activation energies (E_a) of E_a = 10 and 245 meV were obtained by a linear fitting. The energies represent the acceptor levels formed by the B-doping in the bandgap of β-$FeSi_2$.

In the first principle calculation of B-doped β-$FeSi_2$ [10], it is reported that the B atoms substituted for Si of β-$FeSi_2$ act as an acceptor, while the B atoms substituted for Fe act as a donor. In this study, the B-doped film showed p-type conduction with the activation energies of E_a = 10 and 245 meV. The result indicates that the Si atoms are partially substituted with the doped B, and the acceptor levels are formed. The formation of the shallow acceptor level (E_a =10 meV) might contribute the p-type conduction. But the obtained hole density of 2×10^{17} cm^{-3} was two orders of magnitude smaller than the doped B concentration (4×10^{19} cm^{-3}) in the film. There is a possibility that the existence of B atoms at Fe sites and interstitial sites. But, at present, the reason why the hole concentration is low is unclear, and further studies are necessary to increase the hole concentration. In the temperature dependences of resistivity and mobility, the transition from band conduction to localized conduction did not observed in the B-doped film. The film includes impurities (B, As) with high concentration. As a result, impurity bands are formed in the bandgap, and then, the impurity-band conduction would be dominant in the film.

4. Conclusion

The p-type β-$FeSi_2$ polycrystalline film was grown by RF magnetron sputtering using the B-doped p^+-Si target with Fe chips. The obtained hole density and mobility were 2×10^{17} cm^{-3} and 71 $cm^2V^{-1}s^{-1}$ at RT, respectively. The acceptor levels formed by the B-doping were 10 and 245 meV. The p-type β-$FeSi_2$ film showed the impurity-band conduction at 77−350 K.

Acknowledgment

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References

[1] R. H. Bube, *Photovoltaic Materials* (Imperial College Press, Amsterdam, 1998).
[2] M. Powalla, and K. Herz, Appl. Surf. Sci. **482**, 65 (1993).
[3] See, for example, V. Borisenko, *Semiconducting Silicides* (Springer, Berlin, 2000).
[4] D. Z. Chi, Thin Solid Films **537**, 1 (2013).
[5] K. Okajima, C. J. Wen, M. Ihara, I. Sakata, and K. Yamada, Jpn. J. Appl. Phys. **38**, 781 (1999).
[6] M. Shaban, K. Nomoto, K. Nakashima, and T. Yoshitake, Jpn. J. Appl. Phys. **47**, 3444 (2008).
[7] Y. Terai, T. Higashi, T. Hattori, K. Ogi, and S. Ikeda, Jpn. J. Appl. Phys. **57**, 05DD03 (2017).
[8] Y. Terai, K. Yoneda, K. Noda, N. Miura, and Y. Fujiwara, J. Appl. Phys. **112**, 013702 (2012).
[9] S. Brehme, P. Lengsfeld, P. Stauss, H. Lange, and W. Fuhs, J. Appl. Phys. **84**, 3187 (1998).
[10] J. Tani and H. Kido. Jpn. J. Appl. Phys. **41,** 6426 (2002).