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Reduction of carrier concentrations of β-$FeSi_2$ films by atomic hydrogen-assisted molecular beam epitaxy

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molecular beam epitaxy. The conductivity of β-$FeSi_2$ films changed from *p* to *n*-type, and the carrier concentration decreased drastically from the order of 10^{19} to that of 10^{16} cm^{-3}. These results show that the atomic hydrogen played an important role to decrease the number of Si vacancies acting as acceptors.

Keyword: β-$FeSi_2$; atomic hydrogen-assisted molecular beam epitaxy; carrier concentration

1. Introduction

Various useful semiconductor devices such as lasers, high-frequency transistors, light emitting diodes, photo diodes, and solar cells have been developed for years. However, most of these semiconductor devices include toxic elements such as As and Cd, and rare element such as In. In 1997, the new term “Kankyo Semiconductors” was proposed in Japan. Kankyo semiconductors are semiconductors composed of abundant chemical elements in the earth’s crust. It is of great importance to note that the abundant chemical elements in the earth’s crust are usually non-toxic for human body. Semiconducting β-$FeSi_2$ is one of the most extensively studied Kankyo semiconductors, because it consists of extremely abundant Si and Fe. Very large optical absorption coefficient of over 10^5 cm^{-1} at 1 eV, being equivalent to that of CIGS, features this material [1]. Demonstrations of light-emitting diodes operating at wavelengths used for optical-fiber communication (~1.5 μm) have served to further increase interest in β-$FeSi_2$ [2-6].

β-$FeSi_2$ photodetectors have been prepared by various methods such as ion beam synthesis, sputtering and others. However, the reported external quantum efficiencies have been very small [7,8]. On the other hand, the photoresponsivity reached 58 mA/W at 1.31 μm for Al/n-β-$FeSi_2$ Schottky diode using β-$FeSi_2$ single crystals grown by chemical vapor transport [9]. In addition, the diffusion length of β-$FeSi_2$ single crystal was estimated to be 33.4 μm by electron-beam-induced current (EBIC) technique [10]. We think that part of the reasons is the fact that

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undoped β-$FeSi_2$ films have very large hole concentrations typically on the order of 10^{19} cm^{-3} and low mobilities of several tens of cm^2 /V·s, at room temperature [11]. Such a large hole concentration is thought to originate from Si vacancies in undoped β-$FeSi_2$. Therefore, the diffusion length of electrons generated by optical excitation is considered to be extremely short. Moreover, large residual carrier concentration makes it difficult to control the conductivity of β-$FeSi_2$ by impurity doping. Thus, reduction of residual carrier concentration of β-$FeSi_2$ is one of the most important critical steps for improving a quantum efficiency in β-$FeSi_2$ detectors. Atomic hydrogen-assisted molecular beam epitaxy method, in which atomic hydrogens are generated by a hot tungsten filament and supplied to the grown layers, has been reported so far as the method of decreasing the defect densities of III-V compound semiconductors [12]. However, there have been no reports to date on the growth of β-$FeSi_2$ films by atomic hydrogen-assisted molecular beam epitaxy (MBE).

In this paper, we attempted to decrease a residual hole concentration of undoped β-$FeSi_2$ by atomic hydrogen-assisted MBE.

2. Experimental

An ion-pumped MBE system equipped with electron-beam evaporation sources for 10N-Si and 5N-Fe was used in this study. After cleaning *n*-type floating-zone Si(111) substrates with resistivity higher than 3000 Ω·cm at 850 °C for 30 min in ultrahigh vacuum, a well-developed 7×7 reflection high-energy electron diffraction (RHEED) pattern was confirmed. First, an approximately 20-nm-thick highly [110]/[101]-oriented β-$FeSi_2$ epitaxial template was formed at 650 °C by reactive deposition epitaxy (RDE), that is Fe deposition on a hot Si substrate. Then, Fe and Si were coevaporated on the template at 750 °C to form β-$FeSi_2$ continuous films by MBE. The atomic hydrogen is irradiated from the RDE growth to MBE growth. The atomic hydrogens are generated with the hot tungsten filament heated approximately at 1800℃. The hydrogen back pressure was kept constant during the growth process. We have grown three kinds of samples with different hydrogen back pressures of 8×10^{-4} Pa (sample A), 8×10^{-5} Pa (sample B), and without hydrogen supply. Samples were prepared as summarized in Table 1. Finally, ohmic contacts were formed by evaporating 1-mm-diameter Au/Cr electrodes on the β-FeSi2 surface using a metal mask and sintered at 400 °C for 20 min.

The crystalline quality of the films was characterized by RHEED and X-ray diffraction (XRD).The hole density and mobility were measured at room temperature using the Van der Pauw method. The applied magnetic field was 0.54 T normal to the sample surface.

Table 1. Sample preparation: growth thicknesses of RDE and MBE grown β-$FeSi_2$. Cell temperature and back pressure were also specified.

Sample	Substrate	RDE/MBE (nm)	H_2 crackng Cell Temprature (^oC)	Back pressure (Pa)
A	n-type FZ Si(111)	20/560	1800	8×10^{-4}
B		20/260		8×10^{-5}

3. Result and discussion

Figure 1 shows RHEED patterns observed (a) after the RDE growth in sample A, (b) after the MBE growth in sample A, (c) after the RDE growth of sample B, and (d) after the MBE growth of sample B. Streaky patterns and spotty pattern were observed in sample B as shown in Figs. 1(c) and 1(d). On the other hand, streaky pattern was not observed in sample A. This difference is probably due to the difference in hydrogen pressure during the MBE growth between the two samples. We speculate that the hydrogen pressure was one order of magnitude higher in sample A than in sample B, thus, such a high hydrogen pressure deteriorated the epitaxial growth of β-$FeSi_2$ in sample A.

Figures 2 (a) and 2 (b) show the θ-2θ XRD patterns of samples A and B, prepared with different hydrogen back pressures. The diffraction peaks from various planes exist in sample A, showing that β-$FeSi_2$ in sample A was

polycrystalline. On the other hand, in the XRD pattern of sample B, intense peaks of (220)/(202) and (440)/(404) of β-FeSi2 were clearly seen near the (111) and (222) peaks of the Si substrate, respectively. Thus, highly [110] and/or [101]-oriented β-FeSi2, matching the epitaxial relationship of β-$FeSi_2$ on Si(111), was formed in sample B.

Figure 3 shows carrier concentrations and mobilities of those samples measured at room temperature. The β-$FeSi_2$ films grown with atomic hydrogen supply showed *n*-type conductivity. Furthermore, the carrier concentration decreased by three orders of magnitude from 10^{19} to 10^{16} cm^{-3}, when the hydrogen back pressure was 8×10^{-4} Pa. The mobility increased accordingly from 1 to 300 $cm^2/V\cdot s$. The reason for such a high mobility in sample A is the reduction in carrier density; The carrier density of the sample A is much lower than that of sample B. These measured values didn't change even when the thickness of the substrate was decreased from 525 to 150 μm as shown in the inset of Fig. 3, meaning that the contribution of the Si substrate to the Hall measurement was negligible. When the back pressure was increased from 8×10^{-5} to 8×10^{-4} Pa, the carrier density decreased and the mobility increased.

At present, we don't have enough data to discuss the origin of decrease in residual carrier concentration and change of conductivity from *p*-type to *n*-type. Thus, further study will be mandatory to make clear the effect of atomic hydrogen irradiation during the growth of β-$FeSi_2$. However, it can be at least stated that atomic hydrogen played an important role to decrease the number of residual carrier concentrations in β-$FeSi_2$.

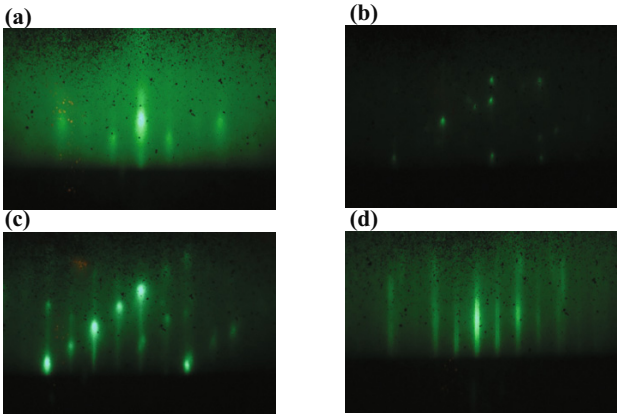

Fig.1 RHEED patterns observed (a) after RDE growth of sample A , (b) after MBE growth of sample A, (c) after RDE growth of sample B, and (d) after MBE growth of sample B.

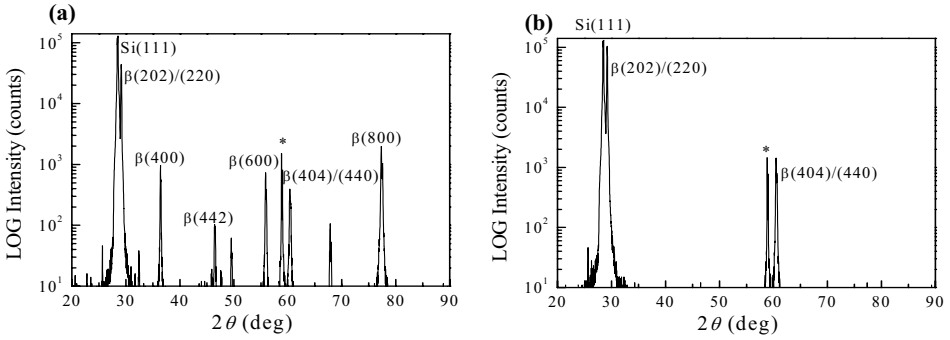

Fig.2 θ-2θ XRD patterns of (a) sample A and (b) sample B.

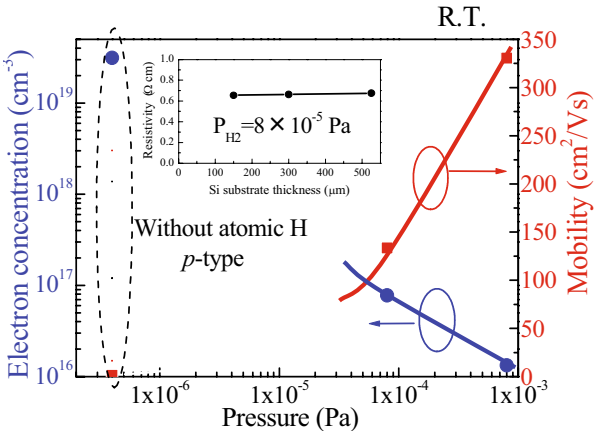

Fig.3 Dependence of carrier concentration and mobility on hydrogen pressure measured at RT. (inset) β-$FeSi_2$ resistivity versus *n*-Si substrate thickness.

4. Conclusions

We have grown intentionally undoped β-$FeSi_2$ thin films on Si(111) substrates by atomic hydrogen-assisted MBE. The conductivity of β-$FeSi_2$ films changed from *p* to *n*-type, and the carrier concentration decreased drastically from the order of 10^{19} to that of 10^{16} cm^{-3}. These results show that the atomic hydrogen played an important role to decrease the number of Si vacancies acting as acceptors.

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