Proc. Asia-Pacific Conf. on Semiconducting Silicides and Related Materials 2016
JJAP Conf. Proc. **5**, 011106 (2017) https://doi.org/10.7567/JJAPCP.5.011106

Dependence of direct transition energy on growth temperature in β-$FeSi_2$ epitaxial films

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(Received April 5, 2017)

Direct transition energy (E_g) of β-$FeSi_2$/Si(111) epitaxial films grown at different growth temperatures (T_s) was investigated by photoreflectance (PR) measurements. In Raman spectra, the wavenumber of A_g-mode in Fe-Fe and Si-Si vibrations shifted to higher wavenumber with decrease of T_s. The estimated Si/Fe composition ratio of the epitaxial layer became small (Si-poor) in the films grown at lower T_s. In PR spectra, E_g shifted to higher energy with decrease of T_s. These results show that the modification of electronic structure by a strain induced at β-$FeSi_2$/Si hetero-interface is suppressed by an increase of Si vacancies in β-$FeSi_2$.

1. Introduction

Semiconducting β-$FeSi_2$ has attracted much interest as silicon-based optoelectronics materials. β-$FeSi_2$ thin films on Si substrate show photoluminescence (PL) at 1.54 μm, which is a wavelength for fiber optics communications [1,2]. The semiconducting β-$FeSi_2$ with orthorhombic structure is formed after a moderate distortion of the CaF_2 structure by the Jahn-Teller effect [3]. Therefore, electronic structure and optical property of β-$FeSi_2$ epitaxial films are considered to be modified by the strain induced at the heteroepitaxial interface of β-$FeSi_2$/Si. The strain effects on the electronic structure have been investigated by first principle calculations [4-8], but there have been no experimental result about the modification of electronic structure. In our recent studies, we have investigated lattice deformations and direct transition energies (E_g) in β-$FeSi_2$ epitaxial films grown on Si(111) substrate, and revealed that the E_g shifted to lower energy by the lattice shrinkage induced by thermal annealing [9,10]. The change of E_g by the lattice deformation is the first result to show the modification of electronic structure by the strain. When defects of Fe or Si are increased in the epitaxial films, a disorder of the atomic arrangement is induced. There is a possibility that the strain at the hetero-interface is relaxed by the disorder, resulting in a suppression of the modification of the electronic structure. The effect of the disorder on the electronic structure should be investigated to control the electronic structure of β-$FeSi_2$ by the strain.

In this study, we have grown the β-$FeSi_2$ epitaxial films on Si(111) substrate at different growth temperatures (T_s) to change the amount of Si vacancies. In the epitaxial films, the effects of Si defects on the E_g were investigated by photoreflectance (PR) measurements.

2. Experiments

The β-$FeSi_2$ epitaxial films on Si were grown by molecular beam epitaxy (MBE) at different T_s with a fixed flux ratio of Si/Fe. The β-$FeSi_2$ template layer of 20 nm was grown on Si(111) substrate by reactive deposition epitaxy (RDE) at T_s = 670 °C. Then, the β-$FeSi_2$ epitaxial films of 60 nm were grown on it by co-deposition of Si and Fe (MBE). The flux ratio of Si/Fe was fixed at Si/Fe = 1.17, and the growth temperature was changed at T_s = 400−670 °C. During the MBE growth, Si atoms are supplied to the β-$FeSi_2$ layer by the molecular beam of Si and a thermal diffusion of Si from Si substrates. When the T_s is decreased at the fixed flux ratio, the thermal diffusion of Si is reduced. As a result, the Si vacancies are increased in the epitaxial layer due to the reduced diffusion of Si. In Raman measurements by semi-backscatter geometry, the Raman lines were excited by a 532 nm laser and detected by a 55 cm focal-length spectrometer with a liquid-nitrogen-cooled CCD. The Si composition in the epitaxial layer was estimated by the scattering intensity of TO phonon line in bulk Si (520.2 cm^{-1}). Detailed direct transition energies E_g were investigated by PR measurements at 11 K. In PR measurements, a halogen lamp in conjunction with a single grating monochromator was used as a probe source. The pump source was a 532 nm laser mechanically chopped at a frequency of 140 Hz. The modulated reflection signal (ΔR/R) was detected by an InGaAs photodiode. The E_g was obtained by the fitting using a generalized Lorentzian function called the Aspnes third derivative functional form [11].

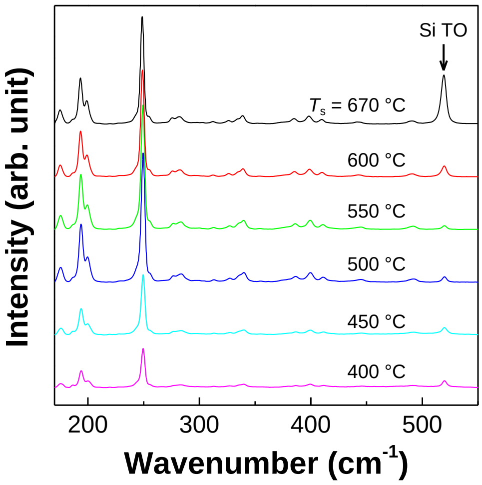

Figure 1 Raman spectra grown at different growth temperatures.

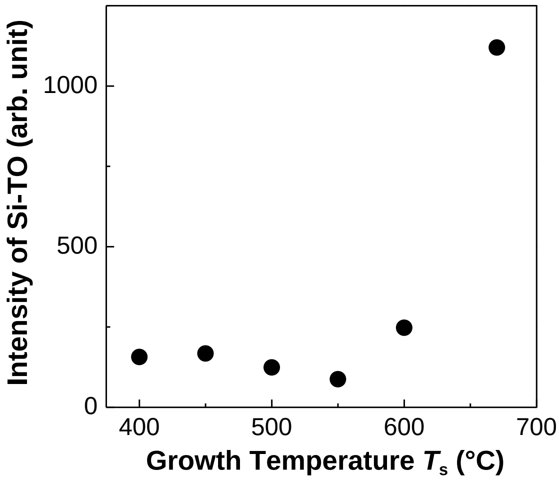

Figure 2 Intensity of Si-TO line as a function of growth temperature.

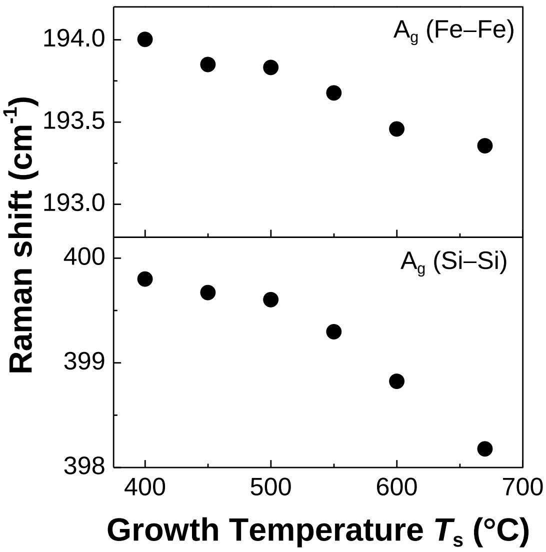

Figure 3 Raman peak positions of A_g-mode as a function of growth temperature.

3. Results and Discussion

Figure 1 shows Raman spectra of the as-grown films grown at different T_s. The Raman lines in 180−500 cm^{-1} were assigned to Fe-Fe, Fe-Si, Si-Si vibrations in β-$FeSi_2$. In the film grown at T_s = 670 °C, a strong Raman line at 520 cm^{-1} was observed. The Raman line is TO-phonon line of bulk Si. The observation of the Raman line at 520 cm^{-1} shows that a microcrystalline silicon is precipitated in the β-$FeSi_2$ film. The peak intensity of Si-TO line is plotted as a function of T_s in Fig 2. The intensity decreased at lower T_s. The T_s-dependence of Si-TO line revealed that the Si composition of the epitaxial layer became low due to the reduced Si diffusion from the Si substrate to the β-$FeSi_2$ layer at lower T_s. In the films grown at T_s = 600, 670 °C which showed a remarkable Si-TO line, the composition ratio was confirmed to be Si/Fe > 2 (Si-rich). In the films grown at T_s = 400−550 °C, the intensity of Si-TO line was almost constant. From the T_s-dependence, the composition ratio was estimated to be Si/Fe = 2 (stoichiometry) at T_s = 550 °C, and Si/Fe < 2 (Si-poor) at T_s = 400−500 °C. The Raman lines at ~194 cm^{-1} and ~400 cm^{-1} are assigned to A_g-mode (breathing mode) of Fe-Fe and Si-Si vibrations in β-$FeSi_2$, respectively. The peak wavenumber of the A_g-mode as a function of T_s is plotted in Fig. 3. The peak positions of A_g-mode shifted to lower wavenumber in the films grown

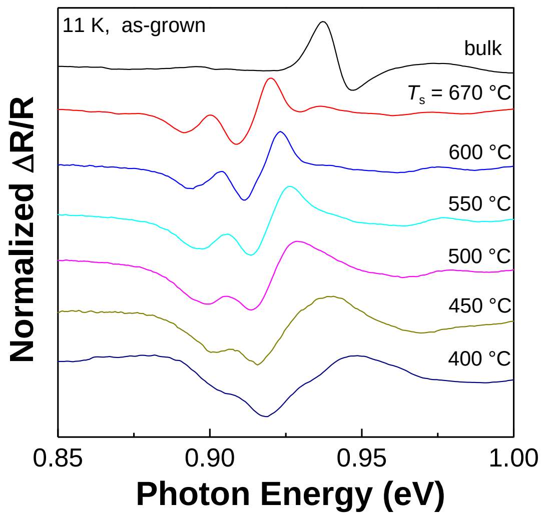

Figure 4 PR spectra of as-grown films.

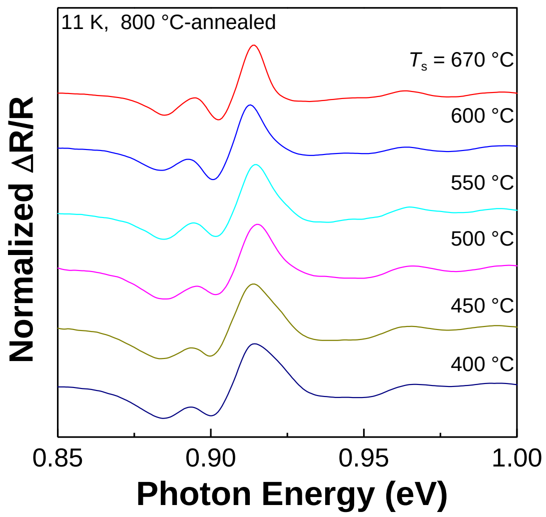

Figure 5 PR spectra of films annealed at 800 °C.

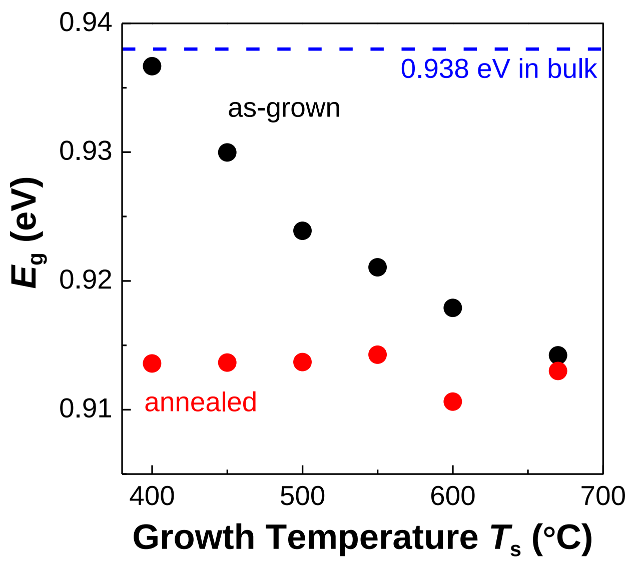

Figure 6 Direct transition energy (E_g) as a function of growth temperature.

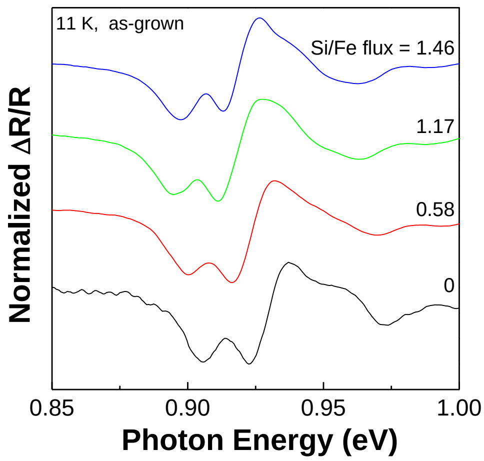

Figure 7 PR spectra of as-grown films.

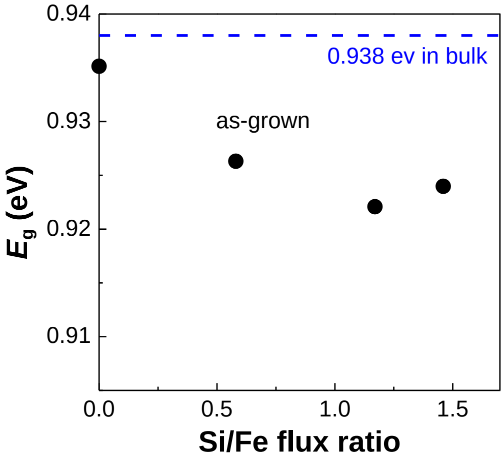

Figure 8 E_g as a function of growth temperature.

at higher T_s. The shift of the Raman lines indicates that the strain around each atoms is changed by the introduced Si vacancies [12].

Figure 4 and 5 show PR spectra of the as-grown films (Fig. 4) and the films annealed at 800 °C for 16 h (Fig. 5). For comparison, PR spectrum of a β-$FeSi_2$ single crystal is also shown in Fig. 4. The samples show the PR spectra with a third derivative functional form which is observed in low-modulation field. Therefore, the PR spectra originate from a direct transition at *Y* point in the Brillouin zone of β-$FeSi_2$ [9,10]. The E_g was obtained by the fitting using the Aspnes third derivative functional form [11]. The T_s-dependence of E_g is plotted in Fig. 6. In the as-grown films, the E_g shifted to higher energy with decrease of T_s, and approached to the E_g of the β-$FeSi_2$ single crystal (0.938 eV). On the other hand, in the annealed-films, the E_g was almost constant at 0.914 eV. In our previous reports about the modification of electronic structure in β-$FeSi_2$, it was found that the E_g in the epitaxial films shifted to lower energy than that in the single crystals with increase of the strain [9,10]. Therefore, the E_g-shift to higher energy with decrease of T_s is understood by the relaxation of the strain due to the disorder of atomic arrangement. In the films grown at lower T_s, the Si/Fe composition ratios became Si/Fe < 2 (Si-poor) due to the reduction of Si-diffusion from the Si substrate. These results show that the Si vacancies induce the disorder of atomic arrangement, resulting in the relaxation of the strain. So, the precise control of Si/Fe ratio is necessary to control the electronic structure of β-$FeSi_2$ by the strain.

In order to confirm that the electronic structure is modified by the change of Si/Fe composition ratio, the β-$FeSi_2$ epitaxial films were grown at 550 °C under different Si/Fe flux ratios of 0−1.46. From the viewpoint of the amount of the Si vacancies, the films grown at low Si/Fe flux ratios correspond to the films grown at low T_s in Fig. 4. Figure 7 and 8 show the PR spectra and the obtained E_g in the as-grown films grown at the different Si/Fe flux ratios. The PR spectra and the E_g shifted to higher energy with decrease of the Si/Fe flux ratio. The result clearly corresponds to the T_s-dependence of E_g in Fig. 6 and supports the relaxation of the strain in the epitaxial films by the Si vacancies.

3. Conclusion

The direct transition energy (E_g) of β-$FeSi_2$/Si(111) epitaxial films grown at different growth conditions was investigated by PR measurements. The E_g of the epitaxial films shifted to lower energy than that of the strain-free β-$FeSi_2$ single crystal due to the modification of electronic structure by the strain. When the Si vacancies in the epitaxial films were increased by the growth at low T_s and low Si/Fe flux ratio, the E_g shifted to higher energy and approached to the E_g of the β-$FeSi_2$ single crystal. These results show that the modification of electronic structure by a strain induced at β-$FeSi_2$/Si heterointerface is suppressed by the increase of Si vacancies in β-$FeSi_2$.

Acknowledgment

This work was supported in part by JSPS KAKENHI Grant Number 26289093.

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