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The effect of crystalline structure on photoluminescence of the \( \beta \)-FeSi\(_2\) film prepared by pulsed laser deposition using two types of target

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Abstract

Ecological friendly \( \beta \)-FeSi\(_2\) thin film has been formed on FZ-Si (111) substrates using sintered FeSi\(_2\) (purity 99.99\%) and electrolytic Fe (purity 99.99\%) targets by pulsed laser deposition (PLD) method in an ArF (\( \lambda = 193 \) nm) excimer laser. Subsequently the prepared thin films were annealed at 900\(^\circ\)C. Cross sectional transmission electron microscope (TEM) results confirmed that the epitaxial growth of the \( \beta \)-FeSi\(_2\) on the thin films and the crystalline structure was improved after increasing the annealing time 5 to 20 hrs ranges using two types of target. It was also showed the polycrystalline structure and the thickness of the thin films were 80 to 100 nm for FeSi\(_2\) target and 200 to 250 nm for Fe target. The TEM result was also confirmed by electron diffraction (ED) method. The intrinsic photoluminescence (PL) intensity of the A-band peak from 20 hrs annealed sample was investigated. A-band peak was considered as the intrinsic band peak because there are another defect related peaks also investigated from the thin films. We report on the effect of the crystalline structure (ECS), luminescence characteristics and band structure condition to apply in solar cell and optical fiber communications.

Keywords: \( \beta \)-FeSi\(_2\), PLD, TEM, Crystalline effect and PL.

INTRODUCTION

Ecological friendly semiconducting silicides \( \beta \)-FeSi\(_2\) has attracted much attention as a candidate for silicon based optoelectronic materials for last couple of decades. Single-phase \( \beta \)-FeSi\(_2\) with high crystal quality fabrication process has chemical and physical stability, absorption coefficient indicating that it has potential as photovoltaic and solar energy cell [1, 2]. \( \beta \)-FeSi\(_2\) has also great potentiality as a silicon-based light emitting material to apply in optical fiber communication [3]. PLD is more appropriate for the preparing epitaxial growth, better crystalline structure and luminescence characteristics of the thin films [4, 5].

In this study, from the viewpoint of future applications to large-scale optical fiber communication, solar cells and light-emitting diodes (LED), we investigated the \( \beta \)-FeSi\(_2\) thin films from last one decade in our laboratory and characterized various experimental and simulation results. We systematically showed the results previously in different publications [6, 7]. In this manuscript, we will show the recent experimental results and research development of the \( \beta \)-FeSi\(_2\) film.

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EXPERIMENTAL PROCEDURE

For the preparation of the semiconducting silicides $\beta$-FeSi$_2$ thin film, the FZ n-Si (111) (1000-2000 $\Omega$cm) substrates were cleaned with organic solvents. The substrates were dipped in a dilute HF solution with a ratio of (HF: $H_2O = 2:40$) for one min. The etched Si (111) substrates were then rinsed in de-ionized water and subsequently loaded into the growth chamber with a base pressure at $10^{-5}$ Pa. The $\beta$-FeSi$_2$ films were prepared at a substrate temperature of 600 °C with the sintered FeSi$_2$ target (purity 99.99 %). On the other hand, we have also prepared the sample by using electrolytic Fe (purity 99.99%) target. The laser source used was an ArF excimer laser (wavelength: 193 nm) and the laser fluence was 4.0 J/cm$^2$. The $\beta$-FeSi$_2$ film was subjected to high-temperature long-time annealing using an infrared lamp in a continuous-gas flow and N$_2$-atmosphere (99.9995 %). Moreover, to improve the crystalline structure quality and to enhance the optical and epitaxial growth of the $\beta$-FeSi$_2$ sample, the as-deposited thin films were annealed for different times. The annealing temperature was 900 °C. In our previous study, we have investigated the phase condition and epitaxial growth by X-ray diffraction method (XRD) [7, 8]. In this study, we have carried out the cross-sectional TEM and electron diffraction (ED) to investigate the effect of the crystalline (ECS) of the $\beta$-FeSi$_2$ thin film using two types target. The temperature dependence PL of 20hrs annealed sample was also examined at temperature ranges of 15 to 160 K. The sample also carried out by single monochromatic and also using a liquid nitrogen cooled InGaAs detector at wavelength of 488 nm line of an Ar ion laser with the focal length 32cm.

RESULTS AND DISCUSSION

For the preparation of the ecological friendly semiconducting silicides $\beta$-FeSi$_2$ thin film, we have carried out the PLD method using two types of targets. The different time dependent annealing samples using electrolytic Fe target and sintered FeSi$_2$ target. Samples 01 and 02 were deposited by electrolytic Fe (99.99%) for 5 and 20 hrs annealed at 900°C. Samples 03 and 04 were deposited by sintered FeSi$_2$ target and also annealed at the same condition of sample 01 and 02. The investigation of the epitaxial growth and the crystalline properties of the thin films are essential of the $\beta$-FeSi$_2$ films for the application in solar energy and optical fiber communications. In these aspects, we have carried out the XRD [7] shown in our previous study. Therefore, we have confirmed the epitaxial growth in $\beta$-FeSi$_2$ film investigated. However, the ECS could not be investigated by XRD measurements. To investigate the crystalline condition on the sample, we have performed the cross-sectional TEM to confirm the epitaxial growth and crystalline structure of the thin films. TEM shown in Figures 1(a) and 1(b). First, the thickness of the 5 and 20 hrs annealed samples are 250 nm and 200 nm respectively. The polycrystalline structures were observed in the films. Finally, in the contrast or boundary, we have also found the SiO$_x$ layer of the thin film.

Figures 1(a) and 1(b) Cross sectional TEM of the 5 and 20 hrs annealed at 900 °C of the $\beta$-FeSi$_2$ thin films of Fe$_2$ target oriented sample measured at 50 nm scale.

Figures 2(a) and 2(b) show the cross-sectional TEM of the sintered FeSi$_2$ target oriented samples annealed for 5 and 20 hrs. The thickness of the 5 and 20 hrs annealed samples are 100 and 80 nm respectively. The polycrystalline structures of the thin films were investigated. If we consider the figs 2(a) and 2(b), we clearly observed the enhanced crystallinity in the film structure for the 20 hrs annealed sample as compared with 5 hrs annealed sample. Therefore long time thermal annealing condition of the samples would be suitable for the better crystalline structure of the thin films. A SiO$_x$ layer on the boundary is also observed of the $\beta$-FeSi$_2$ films from all samples. In 5hrs annealing condition the SiO$_x$ was not clearly observed but after increasing the annealing time up to 20 hrs, a clear layer was found on the interface/boundary between the thin film and Si substrate. Above the discussion of the TEM results we have confirmed that lattice growth of the film due to clear contrasts.
attributed to existence of 90° order domains which suggests the sufficient relaxation of the lattice strains in the film [9]. After long time annealing of the thin film the crystalline progress were enhanced near the interface/boundary. Finally the thickness of the thin film became decrease due to diffusion of the Si atoms. These structural effect influences to the intrinsic PL properties will show in Fig. 4. Moreover it is also appeared the lattice pattern around 10 to 15 nm size in each film of figs 2(a) and 2(b). It is noted that there was no remarkable lattice pattern observed on the sample 01 and 02. Therefore we have picked up the lattice pattern and enlarged the images of the film. Figures 3(a) and 3(b) show the lattice pattern images of the sample 03 and 04 at in enlarged condition of the thin films and confirmed the ECS of the β-FeSi₂ thin films.

Figure 3 the enlargement TEM images of the lattice pattern position of the annealed samples (a) 5hrs and (b) 20 hrs

Each pattern can be considered as single crystalline structure of the film whereas the accumulated pattern could be considered as the polycrystalline structures of the thin films. From the above the discussion of the TEM results we have confirmed that lattice growth of the film due to clear contrasts attributed to existence of 90° order domains which suggests the sufficient relaxation of the lattice strains in the film. After long time annealing of the thin film the enhancement of the crystallinity were occurred near the interface/boundary. Finally the thickness of the thin film became decrease due to diffusion of the Si atoms. To investigate the ECS and condition of the β-FeSi₂ films we have also prepared the film by using the electrolytic Fe target and studied the cross sectional TEM. After comparing the TEM result of the both FeSi₂ and Fe target oriented samples, it is clearly investigated that the enhanced ECS were investigated by FeSi₂ target oriented films. This result also confirmed by the electron diffraction (ED) measurements although not shown in this article. The 20 hrs annealed sample showed the improvement of the epitaxial growth and crystalline effect of the β-FeSi₂ films. These structural effects influence the photoluminescence properties of the film. In our previous study we have performed the temperature dependent luminescence properties of the β-FeSi₂ films for the FeSi₂ target. In this study to investigate the comparison between sintering FeSi₂ and electrolytic Fe target of the luminescence properties. Figure 4 shows the PL spectra at 15 K for the thin films prepared using the sintered FeSi₂ and electrolytic Fe targets at a growth temperature of 600 °C and then annealed at 900 °C for 20 hrs.
Maeda and co-workers [4, 9] reported on the basis of IBS results that the PL spectrum at the A-band of 0.803 eV is the intrinsic luminescence of β-FeSi₂, the B-band of the PL progress were occurred near the interface. Finally the spectrum at 0.85-0.87 eV is caused by radiative defects and the C-band of the PL spectrum at 0.75-0.78 eV is caused by impurity band transition in β-FeSi₂ thin film. We reported the PL spectra of the high-temperature and long time annealed β-FeSi₂ thin films prepared using the sintered FeSi₂ target [10, 11]. The PL spectra of the thin films prepared using the sintered FeSi₂ and electrolytic Fe targets also had A, B and C-bands. The main peak (A-band) of the PL spectra in Fig. 4 was near the dislocation-related D₁ lines. Therefore, we investigated the main peak energies of the thin films prepared using the sintered FeSi₂ and electrolytic Fe targets at a growth temperature of 600 °C and then annealed at 900 °C for 20 hrs, in order to distinguish between the intrinsic A-band luminescence from β-FeSi₂ and defect-related luminescence, such as that related to the dislocation-related D₁ lines. First, Figure 5 show the dependence of the main peak energy $E_p(P)$ on the excitation power density ($P$) for both thin films. The PL peak energy at 15 K for the thin film prepared using the sintered FeSi₂ target marked at square block showed a very small dependence within the range of 2 meV on $P$. On the other hand, that for the thin film prepared using the electrolytic Fe target marked at solid round showed a relatively large dependence within the range of 7 meV on $P$. It is noted in our previous study [9] we have showed the resolution data of the excitation power density of the β-FeSi₂ thin film. Now assuming the inter band transition between the conduction and valence bands of β-FeSi₂, $E_p$ should not depend on $P$. Therefore, it was considered that the main peak of the PL spectrum of the thin film prepared using the sintered FeSi₂ target was the intrinsic luminescence of β-FeSi₂ thin film. The temperature dependence of the main PL peak energy ($E_p$) for both thin films was employed by empirical law (Varshini’s formula) to analyse the obtained results.

$$E_p(T) = E_p(0) - aT^\alpha/b + T$$

Where $E_p(0)$ is the peak energy at 0 K, $\alpha$ is the energy shift for temperature, and $\beta$ is a constant. We determined that Varshini’s parameters are $E_p(0)=0.8085$ eV, $\alpha=1.8 \times 10^{-5}$ eV/K, and $\beta=300$ K for the thin film prepared using the sintered FeSi₂ target, and $E_p(0)=0.8115$ eV, $\alpha=3.4 \times 10^{-5}$ eV/K and $\beta=300$ K for the thin film prepared using the electrolytic Fe target. Maeda etal and Martinelli etal [9, 12] reported $E_p(0)=0.803$ eV, $\alpha=1.4 \times 10^{-5}$ eV/K, and $\beta=300$ K for IBS β-FeSi₂ sample, and $\alpha=4.9 \times 10^{-5}$ eV/K and $\beta=360$ K for a Si-implanted Si sample, including high-density dislocations and stacking faults. The results obtained in this study are very close to the results for IBS samples. Moreover, the $\alpha$ obtained in this study is smaller than that of their Si-implanted Si sample. From the results shown in Fig. 5 and equation 1, it was found that the main peak of the PL spectrum of the thin film prepared using the sintered FeSi₂ target was the intrinsic luminescence of β-FeSi₂. The different PL behaviours between the thin films prepared using the sintered FeSi₂ and electrolytic Fe targets were occurred from the difference between the crystalline structures shown in Fig 2 and 3. Finally the enhanced PL peak was obtained from the 20 hrs annealed sample from the both target oriented samples.

CONCLUSION

In this study we have investigated the ecological green semiconductor β-FeSi₂ films prepared by PLD method using two types sintering FeSi₂ and electrolytic Fe target. The cross sectional TEM analysis showed the poly crystalline structures of the thin films were investigated. It is clearly observed that the enhanced crystalline structure from the 20 hrs annealed sample comparing with 5 hrs annealed sample from the both target oriented thin film. This crystalline structure effect influenced the luminescence properties of the β-FeSi₂ films. In the PL measurements, we have investigated the strong and intrinsic luminescence band peak.
from FeSi$_2$ target deposited thin films. This result obtained due to high crystalline effect of the sintering FeSi$_2$ deposited thin film comparing with electrolytic Fe target. Moreover we have also calculated very small energy shift $\Delta$ value has been obtained comparing the results of other groups and can be ascribed the intrinsic PL (A-band) of the $\beta$-FeSi$_2$ by PLD. These results also can be compared with other semiconducting materials which are presently using in the fabrication of the photovoltaic, solar energy and optical fiber communications. From the results of TEM and PL measurements it can be considered that the $\beta$-FeSi$_2$ film is highly effective materials for the application in solar energy and optical fiber communications in near future.

References