The effect of target-substrate distance on surface morphology and properties of β-FeSi₂ films prepared by pulsed laser deposition

Yuying Ma¹, *, Linhua Liu ², Xiankun Ren ², and Aihua Liu ³

1 Shandong Kaiwen College of Science & Technology, Jinan, China.
2 Shandong Linuo Solar Power Holdings Co., Ltd, Jinan, China.
3 College of Physics and Electronics, Shandong Normal University, Jinan, China.

*Corresponding author e-mail: mayuying@yeah.net

Abstract. Semiconducting iron disilicide (β-FeSi₂) has been studied as thermoelectric materials, ferromagnetic materials and also optoelectronic materials. Since β-FeSi₂ was successfully fabricated on Si (100) substrate by pulsed laser deposition (PLD) and followed annealing, we investigated the structural properties and crystallographic orientation of the films by X-ray diffraction (XRD) analysis. And also the scanning electron microscopy (SEM) was used to determine the structural properties and surface images of the films. Typical XRD patterns of the films show that no other diffraction peak can be found except β-FeSi₂ and Si. The SEM results show that the films are composed of well-distributed grains, in the range of 100 – 200 nm in diameter. Atomic force microscope (AFM) and Fourier transform infrared (FTIR) spectroscopy were also used to characterize the fabricated β-FeSi₂ films. We can find the roughness of the films and want to get the optimum conditions for the preparation of β-FeSi₂ films on Si (100) substrate by PLD.

1. Introduction
The development of environmental friendly metal-silicide semiconductor materials is important to solve environmental issues such as environmental pollution and resource scarcity. Beta phase iron disilicide, β-FeSi₂, is considered to be ecologically-friendly materials for its component elements are nontoxic and abundant in the earth’s crust [1]. Also β-FeSi₂ is a promising and attractive material for being used in silicon-based optoelectronics due to its excellent electronic and optical properties. For its optical direct band gap is about 0.80-0.89 ev [2], corresponding to a wavelength of 1.5 μm luminescence, which is close to the minimum absorption windows of the silica-based optical fibers [3]. The semiconducting β-FeSi₂ has been intensively studied for light emission devices. Moreover, it is investigated as a high-efficiency material in solar energy conversion cells and photo-detectors for its high photoelectric conversion efficiency of 16-23% and large optical absorption coefficient [4].

In addition, the properties of good chemical - physical stability at high temperature, high resistance to oxidation, and can be grown on Si substrates make it possible to prepare β-FeSi₂ films on Si substrates. It was reported that β-FeSi₂ (100) thin films were possible to grow epitaxial on the (100)
silicon substrates by considering a fact that the lattice mismatch between the films and the substrates is less than 5% [5].

Till now, many kinds of film-growth methods have been used to fabricate β-FeSi$_2$ films on silicon, such as ion-beam synthesis (IBS), chemical vapor deposition (CVD), RF-magnetron sputtering deposition, solid phase epitaxy (SPE), reactive deposition epitaxy (RDE), metal organic vapor phase deposition (MOCVD), molecular beam epitaxy (MBE), pulsed laser deposition (PLD) [6], etc.

However, each method has its drawbacks, for example: (1) Non-epitaxially growth of IBS and high temperature of CVD, (2) RF-magnetron sputtering is not suitable to sputter ferromagnetic materials and SPE method limits the β-FeSi$_2$ film’s thickness, (3) The films obtained by RDE method have poor morphology and the purity of epitaxial layers obtained by MOCVD was degraded. (4) The films grown by MBE method are polycrystalline, and the oval and long-shaped defects exist on the surface of the films. Moreover, the above methods require a post-growth annealing process to complete the chemical reaction or to improve the crystal quality [7].

PLD is one of the extremely versatile methods of fabricating variety of thin films, for the following reasons: (1) The deposition conditions are easily controlled, (2) It has good ability of guaranteeing the ingredient, (3) The deposition rate is high, the test cycle is short, the requests of low substrate temperature and the preparation thin film is even, (4) Prepare and clean processing is simple, it is easy to prepare many kinds of membranous materials. In this paper, we report the simple synthesis method for the β-FeSi$_2$ films, which overcomes the shortcomings of previous preparation methods. PLD is one of the useful ways to synthesize β-FeSi$_2$ films, it reduces the oxidation probability of the β-FeSi$_2$ films. Since the Fe is easily bing reacted with oxygen in the air, we deposited and annealed the films at the growth chamber. Many researchers have devoted efforts to fabricate the epitaxial iron silicides on the Si substrate using this technique [8-10].

As it was reported that the properties of the β-FeSi$_2$ films are depend on the surface conditions of the films and the deposition methods. It is very important to find out the appropriate method and the experimental conditions for the preparation of the β-FeSi$_2$ films with good surface morphologies.

In this paper, we changed the deposition conditions of distance between target and substrate (Dt-s) to obtain the preferentially β-FeSi$_2$ thin films on Si (100) substrates by PLD with an Nd:YAG pulsed laser. The β-FeSi$_2$ films were obtained at a substrate temperature of 650 °C, and situ-annealing temperature of 800 °C. The structural properties, crystallographic orientation and the surface morphology of the films are investigated by X-ray diffraction (XRD), the scanning electron microscopy (SEM), Atomic force microscope (AFM) and Fourier transform infrared (FTIR) spectroscopy.

2. Experimental procedure

Before the deposition, the p-Si (100) (1000-2000 Ω ∙ cm) substrates were cleaned with organic solvents. After being rinsed with high-purity water, the substrates were dipped in a dilute HF solution with a ratio of (HF: H$_2$O=1:20) for 30 min to remove the Si oxides of the substrates. The etched Si substrates were then rinsed in deionized water and subsequently loaded into the growth chamber. We should choose target-substrate distance (Dt-s) of 30 mm, 35 mm, 40 mm, 45 mm, 50 mm respectively. The base pressure of the chamber is 1.1 × 10Pa. The β-FeSi$_2$ films were then deposited at a substrate temperature of 650 °C for 30 min. The target is high purity metallic Fe target (99.999%). The laser source used was an Nd: YAG pulsed laser (wavelength: 1064 nm), the laser energy is 250 mJ with a repetition frequency of 10 Hz. In order to improve the crystalline structure quality and to enhance the optical and epitaxial growth of the β-FeSi$_2$ samples, we annealed the β-FeSi$_2$ samples for 3 h at 800 °C in the vacuum in order to avoid the oxidation and to remove the lattice mismatch brought by substrate defects of the β-FeSi$_2$ films.

The crystalline quality and the structural properties of the thin films were characterized by XRD (A Rigaku D/max-rB X-ray diffraction meter with Cu Kα -line), and the components of the films were analyzed from the results. The surface morphology of the thin films was characterized by SEM (Hitachi
S-570) and AFM (PARK Autoprobcp), and the surface roughness was given at the same time. The Fourier transform infrared spectra were measured using a TENSOR27 FTIR spectrometer at room temperature under the vacuum.

3. Experimental procedure

3.1. XRD analysis
We will show the structural properties and the crystallographic orientation of the samples of the $\beta$-FeSi$_2$ films deposited at different target-substrate distances. Fig. 1 shows the typical XRD patterns of $\beta$-FeSi$_2$ films deposited on the Si (100) substrate kept at the conditions above. Almost all of the diffraction peaks in all patterns are assigned as those of $\beta$-FeSi$_2$ besides Si (400) and Si (200) peaks. We can clearly see the dominant peak of (202/220) and the weak peaks of (331/133), (422/242), (040), (041), (042) from the XRD patterns. There are no obvious signal peaks of other iron silicides and correlated phases, indicating that the single-phase, orthorhombic, $\beta$-FeSi$_2$ thin films have been prepared on the Si (100) substrate using PLD in our experiments. We have obtained the Full Width at Half Maximum (FWHM) value of the (202/220) peaks of the films are 0.157, 0.169, 0.134, 0.168, and 0.170 separately. We can find the intensities of the $\beta$-FeSi$_2$ (202/220) improved from 30 mm to 40 mm, but decreased when Dt-s changed into 45 mm. And the FWHM value of $\beta$-FeSi$_2$ (202/220) is contrary. But when the Dt-s changed to 50 mm, the intensity and the FWHM value increased significantly, So we can conclude the crystallographic orientation of simple at 40 mm is the best.

![Figure 1. The XRD patterns of the $\beta$-FeSi$_2$ films deposited with different target-substrate distances: (a) 30 mm, (b) 35 mm, (c) 40 mm, (d) 45 mm, (e) 50 mm.](image)

3.2. SEM and AFM analysis
The surface morphology of the film is very important for optical applications. During the deposition, the iron reacts with the silicon substrate, which influences the film morphology. The surface morphology of the films were analyzed using SEM and AFM. Fig.2 and Fig.3 showed the SEM and AFM results obtained at five different target-substrate distances of 30 mm, 35 mm, 40 mm, 45 mm, 50 mm, respectively. It can be observed that the films are composed of well distribute nano-particles, in the range of 100-200 nm in diameter. After comparing the five SEM pictures we can conclude that there are not only the nano-particles but also some maze structure and hole shapes on the surface. From figure (a), many holes can be found on the surface, and the particles are the biggest comparing with others, but
the holes on the surface decreased as the distance increased. We can also easily found there are maze-structure turned up when the Dt-s is 35 mm, but disappeared at 50 mm. the particles of the film in (c) is smaller and the particles arranged closly.

The smoothness of $\beta$-FeSi$_2$ films can also be got from AFM images. The average roughness of the films are: (a) 17.0 nm, (b) 15.1 nm, (c) 12.1 nm, (d) 13.6 nm, (e) 12.6 nm, respectively, so the third simple is the most smooth one we get. Also we can easily found that the grains of sample (a) are the biggest among the five samples, and the grains are uneven. The surfaces become much smoother when the Dt-s is changed from 30 to 40 mm, and the average roughness increased when Dt-s is up to 45 mm decreased to 50 mm. The AFM result is agreed well with the SEM results, so we can find the Dt-s is the best one of our experiment.

![SEM patterns of the $\beta$-FeSi$_2$ films deposited with different target-substrate distances](image)

**Figure 2.** SEM patterns of the $\beta$-FeSi$_2$ films deposited with different target-substrate distances of (a) 30 mm, (b) 35 mm, (c) 40 mm, (d) 45 mm and (e) 50 mm.
Figure 3. AFM patterns of the $\beta$-FeSi$_2$ films deposited with different target-substrate distances of (a) 30 mm, (b) 35 mm, (c) 40 mm, (d) 45 mm and (e) 50 mm

3.3. FTIR analysis
The FTIR spectra measurements were carried out to identify the phase and characterize the crystal quality, the results are showed in Fig.4. From the spectra, we can find the obvious peaks at about 261.8 cm$^{-1}$, 297.9 cm$^{-1}$, 311.0 cm$^{-1}$, 345.6 cm$^{-1}$, 425.4 cm$^{-1}$, respectively, which can be contributed to the infrared vibrations of $\beta$-FeSi$_2$ [11]. Comparing the five simples, we can see the FTIR peaks shift to a higher wave number with the increase of the distance. The relative absorbancy of simple (c) and (d) are nearly the same but the absorption decreased a lot from (d) to (e). Especially the simple(c), the FTIR spectra changed a lot, the increase of the corresponding absorption is the most apparent in five samples. Though it is difficult to form single-phase $\beta$-FeSi$_2$ films by diffusion of iron and silicon atoms, we can find that we have obtained the single-phase $\beta$-FeSi$_2$ films with after situ-annealing.

Figure 4. The FTIR spectra of the simples deposited under the conditions of different Target-substrate distances: (a) 30 mm, (b) 35 mm, (c) 40 mm, (d) 45 mm, (e) 50 mm.

3.4. Discussion
We think all phenomena is related to the relationship of Dt-s and the length of plasma (Lp). The kinetic energy of the particles in the plasma are different along with the plasma. When Dt-s is much shorter than the value of Lp, the particles of the plasma with high kinetic energy are large and can be easily reflected only left the holes on the surface, the compactness of $\beta$-FeSi$_2$ films become better when the
distance increased from 30 mm to 40 mm. Also the crystalline quality from XRD, FTIR spectra show the same trend. But films grown on the surface of the substrate further hampered the reaction of Fe particles with Si on the surface of substrate. So the XRD intensity and the FWHM value changed a lot when the Dt-s changed to 45 mm.

The abnormal phenomena of XRD (Dt-s=50 mm) can be explained by the concentration of particles from plasma tail is low and these particles also have low kinetic energy, Once Dt-s is longer the number of laser excited particles reached and adsorbed to the substrate surface only by physical adsorption and don't move randomly[12]. But the particles can react with the Si on substrate to form the $\beta$-FeSi$_2$ films during situ-annealing. The low kinetic energy and low surface migration rate lead to the thinner films, So we can get the abnormal SEM, AFM, XRD results at Dt-s=50 mm.

4. Conclusion
We have obtained high quality $\beta$-FeSi$_2$ films without any fragments by pulsed laser deposition on Si (100) substrate at growing temperature of 650 $^\circ$C and situ-annealing temperature at 800 $^\circ$C. The XRD results reveal that the crystal phases of the composite film are $\beta$-FeSi$_2$, and there is no other phases besides Si and $\beta$-FeSi$_2$. These results confirm the successful fabrication of $\beta$-FeSi$_2$ films by diffusion of Fe atoms to Si(100) substrate using PLD technology. The SEM results of the prepared films indicate that the surface is smooth, and the particles are uniform.

As a conclusion, the film fabricated at the distance of 40 mm is the best. So the Dt-s of 40 mm is regarded to be a proper distance to prepare $\beta$-FeSi$_2$ films by the Fe target at 650 $^\circ$C, 1.1 × 10$^{10}$Pa for 30 min, and situ-annealed in the PLD setup at 800 $^\circ$C for 3 h.

Acknowledgments
This work was financially supported by Shandong kaiwen college of Science & Technology’s campus fund project, The research of solar photovoltaic and solar-thermal systems (numbered:kwz201805) fund.

References
[1] Y. Makita, AIP Conf. Proc. 404 (1997) 3.
[2] M.C. Bost, J.E. Mahan, J. Appl. Phys. 64 (1988) 2034.
[3] M. Zakir Hossain, Tomohiro Mimura, Noboru Miura, Shin-ichiro Uekusa Appl. Surf Sci. 256 (2009) 1227 - 1231
[4] S.Y. Jia,, G.M. Lalevb, J.F. Wang, J.W. Lima, J.H. Yooa, D. Shindoa, M. Isshiki, J. Cryst. Growth. 285 (2005) 284 - 294.
[5] M Tode, Y Takigawa, M Ohmukai, K.Kurosawa and M Muroya.J. Phys.: Condens. Matter. 59 (2007) 376 - 379
[6] N. Dmitruk, L. Dozza, S. Mamykin, O. Kondratenko, G. Molnar. Vacuum 84 (2010) 238 - 242
[7] S.Y. Jia,, G.M. Lalevb, J.F. Wang, J.W. Lima, J.H. Yooa, D. Shindoa, M. Isshikia, M. Uchikoshi, M. Isshiki, Mater. Lett. 59 (2005) 2370.
[8] Y. Nakamura, Y. Nagadomi, S.P. Cho, N. Tanaka, M. Ichikawa, Phys. Rev.B 72 (7) (2005) 075404.
[9] J.H. Won, K. Sato, M. Ishimaru, Y. Hirotsu, J. Appl. Phys. 100 (1) (2006) 14307.
[10] L. Dozza, G. Molnar, Z.J. Horvath, A.L. Toth, J. Gyulai, V. Raineri, F. Giannazzo, Appl. Surf. Sci. 234 (2004) 60.
[11] R. Ayache, A. Bouabellou, E. Richter, Mater. Sci. Semicond. Process. 7 (2004) 463.
[12] Daoren Gong, Dongsheng Li, Zhizhong Yuan, Minghua Wang, Deren Yang,Appl. Surf. Sci.254 (2008) 4875-4878.