Effect of the growth temperature on the surface characterization of β-$FeSi_2$ films prepared by pulsed laser deposition

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The β-$FeSi_2$ films were successfully fabricated by pulse laser deposition on silicon (100) in a wide range of growth temperature. The crystalline structures of the films were measured by using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). It shows that crystalline quality of the films has improved with the increase of the growth temperature and the (331)-orientated monocrystal β-$FeSi_2$ films are obtained at the growth temperature of 800 °C. The surface properties of the films were characterized with scanning electron microscopy (SEM). The smooth surface of the films was acquired at 750 °C-800 °C. It is found that both the crystal orientation and surface morphology of the β-$FeSi_2$ films were associated with growth temperature.

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1. Introduction

In the past decade, semiconducting β-$FeSi_2$ attracted much attention due to its theoretical direct band gap of 0.85 eV, which fits transmission window of silica based optical fiber [1-5]. It was also further studied as a candidate for application to the optoelectronics devices with the well compatibility with silicon technology. Because of the large absorption coefficient ($\alpha>10^{-5}$ cm^{-1} at 1.0 eV), β-$FeSi_2$ is expected to be a candidate for a new solar cell material [6, 7]. Furthermore, it has much superior features such as chemical stability, non-toxicity and its components are abundant on the earth, which as well favor the use of β-$FeSi_2$ as a new type of environmentally friendly material. The semiconductor silicon element has a considerable role within the technology of photovoltaics. Silicon-based photovoltaic devices are preferable due to their stable chemical properties and their consistency with the technology of microelectronics [8]. However, in contrast to the excellent theoretical properties of β-$FeSi_2$ material, few practical results have been achieved in experiments due to the poor film quality.

Up to now, many growth methods have been explored to fabricate the β-$FeSi_2$ films on Si substrate, including reactive deposition epitaxy (RDE) [9, 10], ion beam synthesis (IBS) [11, 12], solid phase epitaxy (SPE) [13, 14], molecular beam epitaxy (MBE) [15-17] and pulsed laser deposition (PLD) [18, 19], etc. These efforts have contributed to the improvement of the β-$FeSi_2$ film quality. S. Matsumura, et al., reported the monocrystal β-$FeSi_2$ films achieved by MBE [16]. However, the MBE equipment is very expensive. So it is necessary to look for other economical techniques to prepare β-$FeSi_2$ film. In this work, the β-$FeSi_2$ films were prepared through depositing iron atoms on silicon substrates by PLD. The PLD is an extremely successful method in fabricating a wide variety of thin films and its deposition conditions are easily controlled. The high quality β-$FeSi_2$ film was obtained by this method in our previous work [18].

In this study, the β-$FeSi_2$ films were prepared by depositing iron atoms on silicon substrates with a PLD technique following 3 h post-growth in situ at different temperature. The momocrystal β-$FeSi_2$ film was obtained at the growth temperature of 800 °C. Moreover, the crystalline structure and the morphology of the films were characterized, and the film growth mechanism was discussed briefly.

2. Experimental procedure

For the preparation of crystalline β-$FeSi_2$ films, the Fe target (99.999%, dimensions 5×4×0.3 cm) were initially cleaned by laser ablation for 3 min under vacuum conditions to remove the surface contaminants. The p-type (100 orientation and resistivity 0.5-0.7 Ω·cm) substrates were cleaned with organic solvents and dipped in a dilute HF (HF: H_2O = 2:40) solution for 1 min to get rid of the native silicon oxide. Then the Fe target was irradiated by an Nd:YAG pulsed laser with a wavelength of 1064 nm in a vacuum chamber with a base pressure of 2×10^{-5} Pa. The growth temperature was set to be 600 °C, 650 °C, 700 °C, 750 °C and 800 °C, respectively and a 3 h post-growth process was performed in situ at the corresponding temperature. The deposited Fe atoms reacted with the diffused Si atoms from the underlying Si substrate to

produce a β-$FeSi_2$ layer. The laser fluence was 7 J/cm^2 and the repetition rate was 10 Hz. The distance between the targets and the substrates was 40 mm. The deposition time was 30 min for all the samples. The crystal quality and the phase of the thin films was measured by Bragg-Brentano X-ray diffraction (XRD, A Rigaku D/max-rB X-ray diffraction meter with Cu Kα-line) and the Fourier transform infrared spectroscopy (FTIR, TENSOR27). The surface morphologies of the thin films were characterized by scanning electron microscopy (SEM, Hitachi S-570).

3. Results and discussion

3.1. XRD analysis

Fig. 1(a-e) shows the XRD patterns of the films prepared at different growth temperature of 600 °C, 650 °C, 700 °C, 750 °C and 800 °C, respectively. It can be seen in Fig. 1 (a-e), apart from the substrate Si (400) peak, all peaks in the diffraction pattern could be identified with the β-$FeSi_2$ [20]. It is implied that the single-phase β-$FeSi_2$ could be synthesized in a wide range of growth temperature. A pronounced β-$FeSi_2$ (202)/ (220), and some weak peaks such as β-$FeSi_2$ (331), (040), (041), (511), (422) (133), (024) and (242) appear in the Fig.1 (a), indicating a polycrystalline structure in nature. As shown in Fig. 1 (a-c), the intensity of the peaks increases and some peaks such as (041), (511), (024) and (242) disappear with the increase of the growth temperature. It is suggested that the films have obtained a more orderly texture with the increase of growth temperature. As can be seen in Fig. 1(d), the crystal orientation changes greatly. The β-$FeSi_2$ (202)/ (220) peak become weak and β-$FeSi_2$ (331) peak increase greatly becoming the dominant one. Moreover, the number of the peak decreases further, indicating that the crystalline quality is becoming better. When the growth temperature reaches up to 800 °C, only a strong β-$FeSi_2$ (331) peak was observed as shown in Fig. 1(e). It is suggested that the film obtain a monocrystal structure. According to the XRD result, one can see clearly that the crystalline quality of the β-$FeSi_2$ film can be improved effectively by increasing the growth temperature.

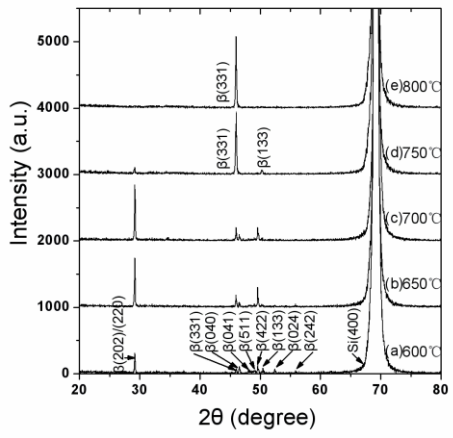

Fig. 1. XRD patterns of the films prepared at different growth temperature of 600 °C(a), 650 °C(b), 700 °C(c), 750 °C(d), 800 °C(e).

3.2. FTIR analysis

Fig. 2(a-e) displays the FTIR spectra for the films at different growth temperature of 600 °C, 650 °C, 700 °C, 750 °C and 800 °C, respectively. All the samples at the different temperature show the similar transmission characteristic in the shape and position. Obvious peaks at about 262, 297, 311, 347, 384 and 425 cm^{-1} are all observed, which can be attributed to the infrared vibrations of the β-$FeSi_2$. These wave numbers are in good agreement with the literature which reported that the β-$FeSi_2$ peaks at about 264, 297, 311, 350, 384 and 425 cm^{-1} [21]. According to the experimental spectra by Guizzeti et al [22], the wave numbers at 311 cm^{-1}, 345 cm^{-1} and at 382 cm^{-1} are along the a-axis. The wave numbers at about 345 cm^{-1} are expected to originate from the counter-phase vibration of Fe and Si atoms and the numbers lower than 300 cm^{-1}, detected at about 262 cm^{-1}, 295 cm^{-1}, are related to the vibration of the Fe-Fe band. At a high frequency, 425 cm^{-1} is attributed to the motion of the Si-Si band [21]. Furthermore, one can see that the intensity of transmission spectra is related to the growth temperature. The films grown at the higher temperature display the stronger transmission intensity. This result reflects that the crystalline quality of the film is improved with the increase of the growth temperature. This conclusion agrees well with the XRD result. The FTIR spectra together with the XRD studies imply the formation of the β-$FeSi_2$ phase.

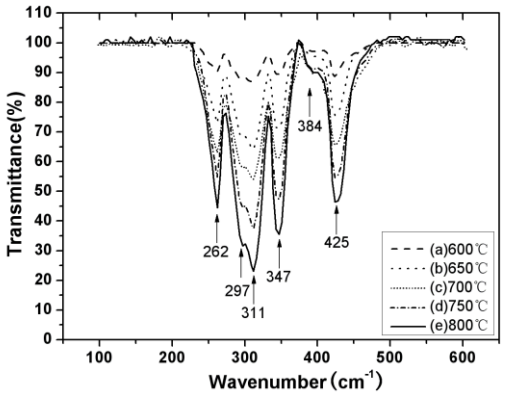

Fig. 2. FTIR spectra for the samples deposited with different growth temperature 600 °C(a), 650 °C(b), 700 °C(c), 750 °C(d), 800 °C(e).

3.3. SEM analysis

Fig. 3(a-e) show SEM images of the samples prepared at different growth temperature of 600 °C, 650 °C, 700 °C, 750 °C and 800 °C, respectively. The film surface in Fig. 4(a) is uneven. It shows some agglomerations with various shapes and sizes. Some white dots marked with circle and holes marked with a rectangle are also observed. Usually, the metal is brighter than the semiconductor under the SEM view, so it can be concluded that the dots are iron particles. It is suggested that the sputtering iron atoms can not fully reacted with the diffused Si atoms from the underlying Si substrate due to the low growth temperature of 600 °C. When the growth temperature reaches up to 650 °C, the white dots and holes disappear, although there still exists some agglomerations with the size of 100-200 nm as

shown in Fig. 4(b). As growth temperature increase further, the film surface becomes much smoother and the agglomerations disappear gradually as shown in Fig. 4(c-e). It can be seen in Fig. 4(d) and (e), the film surface is continuous and uniform, no holes and clusters are found even in a large area, suggesting the improvement of the film quality.

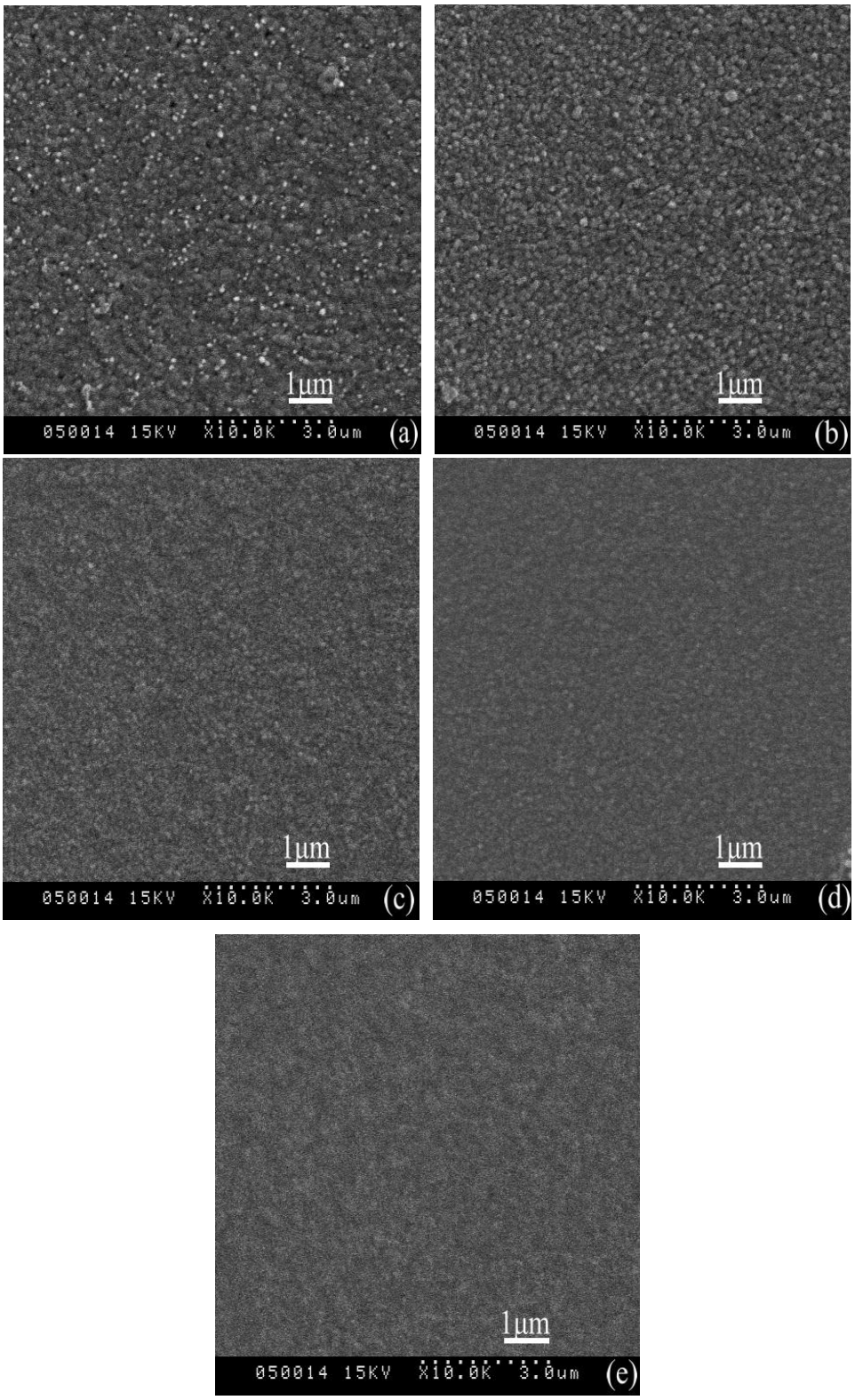

Fig. 3. SEM images of the samples deposited at different growth temperature of 600 ^{o}C(a), 650 ^{o}C(b), 700 ^{o}C(c), 750 ^{o}C(d), 800 ^{o}C(e).

3.4. Discussion of the film growth mechanism

Based on the result, it can be clearly seen that the crystalline quality and the surface morphology have changed a lot with the increase of the growth temperature. The XRD measurement shows that crystalline quality of the films has improved with the increase of the growth temperature. It is also observed that the crystal orientations at above 750 ^{o}C have the preference of β-$FeSi_2$ (331) orientation over β-$FeSi_2$ (202)/ (220) orientation. It is suggested that when the growth temperature is higher than 750 ^{o}C, the surface energy distribution changes. The β-$FeSi_2$ (331) plane replaces β-$FeSi_2$ (202)/ (220) plane and becomes the lowest energy sites. The crystalline grains are likely to grow along the former orientation. At the same time, with the increase of the growth temperature, the film surface has become smoother. It is reasonable to consider that the deposited iron atoms and the silicon atoms can obtain larger kinetic energy at the higher growth temperature. So, the iron atoms are able to react with the silicon atoms fully to produce β-$FeSi_2$ thus no iron particles were observed as shown in Fig. 3(b-e). Moreover, the atoms at the low temperature can not move to the proper sits timely due to the relatively low mobility but covered by the next layer of atoms [23]. As a result, the holds and some agglomerations formed as shown in Fig. 3(a) and (b). On contrary, the atoms at the higher temperature can get a high mobility to migrate along the surface until they reach the lowest energy sites thus form a compact and smooth surface. It is believed that the higher temperature may have accelerated the atom diffusion processes and favored the formation of the ordered structures.

4. Conclusions

The β-$FeSi_2$ films were successfully prepared by pulse laser deposition on silicon (100) in a wide range of growth temperature and the (331)-orientated monocrystal β-$FeSi_2$ films are obtained at the growth temperature of 800 ^{o}C. The XRD and FTIR results show that the film crystalline quality of the films can be improved by increasing the growth temperature. The SEM images display a smooth surface at the temperature of 750 ^{o}C-800 ^{o}C. In conclusion, the quality of the β-$FeSi_2$ films can be improved effectively by increasing the growth temperature.

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