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Fabrication of β-$FeSi_2$ Thin Films by Pulsed Laser Deposition

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Iron silicide thin films were grown by pulsed laser deposition (PLD) using different laser wavelengths (λ = 193 nm, 532 nm, 1064 nm). $FeSi_2$ alloy plate was used as a target. The surface morphology of deposited films was observed using a scanning electron microscope. The films deposited using the 1064 nm and 532 nm lasers showed many droplets with a diameter of 1 ~ 10 μm on the film surfaces in spite of the laser fluence. On the other hand, the films deposited using the 193 nm laser showed no droplets on the film surface at the fluence between the threshold of film deposition, 2 J/cm^2 and that of droplet deposition, 4 J/cm^2. β-$FeSi_2$ thin films were prepared in this fluence range using the 193 nm laser. The film structure of the deposited films was investigated using the X-ray diffraction method and Raman spectroscopy. β-$FeSi_2$ single phase films were grown at a substrate temperature between 200°C and 425°C. At higher substrate temperature, the FeSi phase appeared in addition to the β-$FeSi_2$ phase. The Raman spectra showed two peaks due to the generation of β-$FeSi_2$ at more than 100°C. It is considered that the generation of β-$FeSi_2$ begins at around 100°C in PLD method.

Key words: β-$FeSi_2$, PLD, ablation, semiconductor, thin film

1. INTRODUCTION

Semiconducting β-$FeSi_2$ has excellent properties such as a direct optical band gap of 0.8-0.85 eV,[1,2] a large optical absorption coefficient,[3] good physical-chemical stability at high temperature and high resistance to the oxidation, and the possibility of growing epitaxially on Si substrates.[4] Besides, it overcomes ecological and resources problems because of its nontoxicity and the rich deposits which are present on earth. So it is expected to be a future promising material for Si-ULSI compatible optoelectronics devices, solar cells with theoretical efficiencies from 16 to 23 %,[5] IR photosensors[6] and thermoelectric devices.[7]

β-$FeSi_2$ films have been produced by a variety of methods such as ion beam synthesis,[8,9] reactive deposition epitaxy,[10] solid phase epitaxy[11] and molecular beam epitaxy.[12] In most of these methods, substrate temperature of more than 450°C, and further annealing is necessary in order to obtain a β-$FeSi_2$ film. And it is difficult to prepare single phase β-$FeSi_2$ films because the other iron silicide phases such as α-$FeSi_2$, ε-$FeSi_2$, CsCl-type FeSi and γ-FeSi, all of which are metallic, easily generate in addition to the β-$FeSi_2$ phase. In order to use this β-$FeSi_2$ phase for a variety of applications, a simple preparation method using low substrate temperature, no annealing and independence on the substrate materials, is required.

Pulsed laser deposition (PLD) is a successful method in order to fabricate a large variety of thin films.[13,14] This method is known to have advantages as follows: (a) congruent transfer,[13] (b) crystallinity enhancement due to the high enegretic species,[15] (c) clean deposition due to no atmosphere gas, (d) simplicity and flexibility in engineering design. On the other hand, it has some disadvantages such as the deposition of droplets.[16] The advantages of PLD are very appropriate for the preparation of β-$FeSi_2$ film. But there have been few studies of preparation of β-$FeSi_2$ film using a PLD method.

In this paper, we report the result of a study in which we investigated the condition of depositing the droplet-free films, and at this condition, succeeded in growing the β-$FeSi_2$ phase at low substrate temperature using a PLD method.

2. EXPERIMENT

The experimental schematic for the film deposition is shown in Fig.1. β-$FeSi_2$ films with thickness of 200 ~ 300 nm were deposited on silicon (100) substrates at temperatures in the range of 20 ~ 500°C by the PLD method, using a FeSi alloy target (99.99%) whose composition ratio between Fe and Si was 1:2. The substrates were set parallel with the target at a distance of 25 mm from the target. The laser sources used were an ArF excimer laser (Lambda Physik LPX350ST, λ = 193 nm, 24 ns) and a Q-switched Nd:YAG laser (LOTIS LS-2125, λ = 1064 nm or 532 nm, 13 ns). The irradiation area on the target was approximately 2 mm^2 and the laser fluence F was changed from 1.5 J/cm^2 to 5 J/cm^2 by adjusting the pulse energy. The typical deposition rate was 0.04 nm/sec at the fluence of 2 J/cm^2 using the 193 nm laser. The chamber for the film preparation was evacuated using either a turbo molecular pump or a diffusion pump. The base pressure in the chamber was less than 10^{-6} Torr. The surface morphologies were observed by a scanning electron microscope. The composition of the deposited films was measured with the X-ray photoelectron spectroscopy (Shimadzu ESCA-1000). The crystal structure was studied by the X-ray diffraction method using Cu-Kα radiation. The Raman spectra were measured using a JASCO NRS-2000 instrument.

3. RESULTS AND DISSCUSSION

It is known that the occasional incorporation of spherical particles with a diameter of 1~10 μm, which are ejected from the target due to melting of the surface, can be observed in the deposited films for various materials in PLD methods. These particles spoil strongly the film quality. In this study, before the attempt of preparation of β-$FeSi_2$ thin films, we investigated the appropriate condition in which the films included no droplets. The number of the ejected droplets is thought to depend on the laser irradiation condition because the ejection of the droplet is attributed to the melting of the target surface. Actually, it is reported that the number of the ejected droplets is dependent on the laser fluence in the preparation of the Fe films.[17] Thus, in order to obtain films that did not contain droplets, the appropriate condition of laser wavelength and fluence was investigated. The films deposited using the 1064 nm laser and the 532 nm laser had many droplets in the films, as shown in Fig.1(a) and (b), and this is independent on the fluence. On the other hand, it was found that the films deposited using the 193 nm laser had two thresholds of 2 J/cm^2 and 4 J/cm^2. The former was for depositing the films and the latter was for depositing the droplet. Thus at the fluence between these thresholds, films containing few droplets could be generated, as shown in Fig.1(d). In this study, β-$FeSi_2$ films were prepared within this range of fluence.

The ablation process is composed of several

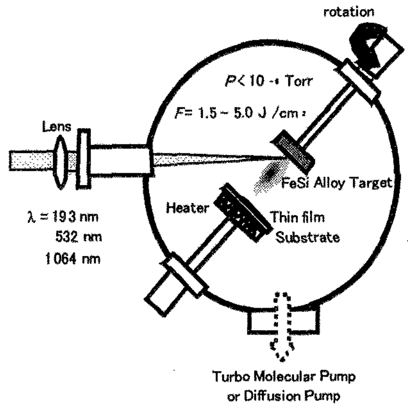

Fig. 1 The experimental schematic for film deposition.

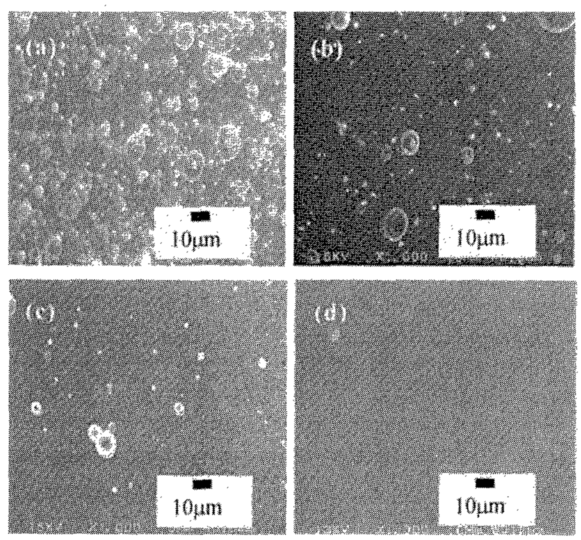

Fig. 2 SEM photographs of the films. (a) λ = 1064 nm, F = 2 J/cm^2, (b) λ = 532 nm, F = 2 J/cm^2, (c) λ = 193 nm, F = 4 J/cm^2, (d) λ = 193 nm, F = 2 J/cm^2.

different effects, the most important of which are a thermal one and a photochemical one. The dependence of the droplet ejection on the laser wavelength and the fluence can be explained as follows. The lasers with long wavelengths, such as 1064 nm and 532 nm, cause ablation due to thermal effects mainly. Consequently, droplets are ejected due to melting of the target surface. On the other hand, lasers with short wavelengths, such as 193 nm, predominantly cause photochemical ablation, where photon energies are expended to excite the electric states of atoms, with the result that the heat for the ejection of droplets does not remain on the target surface. But it increases with the fluence, and thus the droplets begin to be ejected due to the remaining heat at higher fluence.

The composition of the deposited films was measured using X-ray photoelectron spectroscopy. The spectra of the deposited films were nearly the

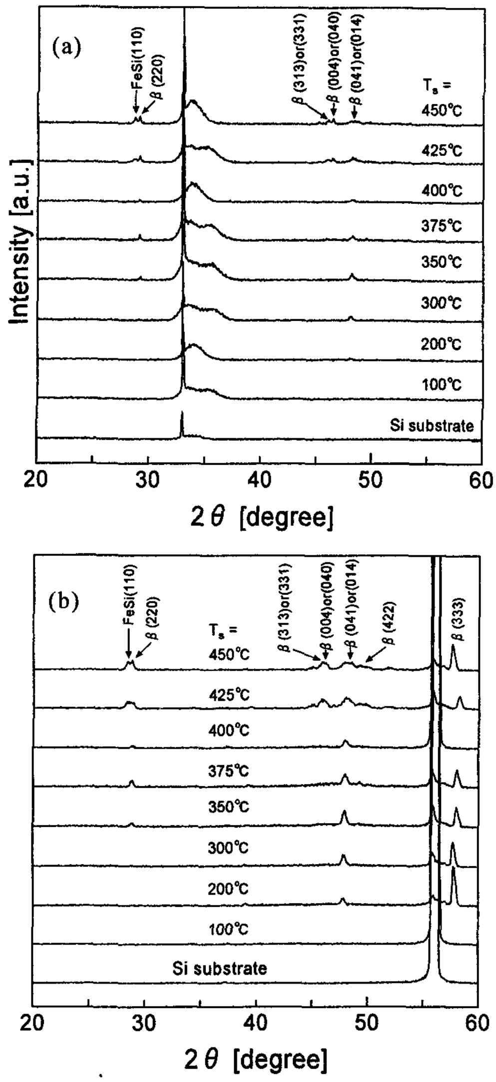

Fig. 3 X-ray diffraction patterns of the films deposited at the various substrate temperature. (a) θ-2θ scan, (b) 2θ scan (grazing incidence).

same as that of the target, and the congruent transfer can be realized to the same levels that have been obtained with other target materials.[13] This is an excellent advantage for the preparation of β-$FeSi_2$ films compared with the other preparation methods.

Fig. 3(a) and (b) show the change in the X-ray diffraction pattern of iron silicide films for various substrate temperatures by 2θ-θ scan and 2θ scan (grazing incidence), respectively. At a substrate temperature of less than 100°C, the films show only a peak due to the substrate. At more than 200°C, the (041) or (014) diffraction peaks of β-$FeSi_2$ can been seen in Fig. 2(a). Fig.2(b) shows the appearance of two peaks of β-$FeSi_2$(041) or (014) and β-$FeSi_2$ (224) or (242). These indicate the generation of β-$FeSi_2$ crystallites at more than 200°C. Their diameter, in the direction of depth, was estimated to be 30 nm by Scherrer's formula.[18] This size is not dependent on the substrate temperature. At more than 350°C, the (220) diffraction peaks of β-$FeSi_2$ appears in both (a) and (b). At more than 425°C, peaks of β-$FeSi_2$ (004) or (040) are observed in addition to the previous diffraction peaks of β-$FeSi_2$. In addition, the diffraction peaks due to the generation of FeSi phase are observed. The FeSi phase begins to be generated at more than 425°C resulting in the double phases films composed of the crystallites of β-$FeSi_2$ and FeSi.

Fig.4 shows the Raman spectra of the deposited films for various substrate temperatures. At the substrate temperature of 20°C, the films did not show any peaks, which is similar to that of the iron silicide target. At more than 100°C, two peaks with centers of 181 cm^{-1} and 239 cm^{-1} due to β-$FeSi_2$ are observed. The positions of these peaks are both lower by approximately 10 cm^{-1} than those of a previous report by another group.[19,20] In addition, all films deposited at more than 100°C shows peak widths of 19 cm^{-1} for the 181 cm^{-1} peak and 15 cm^{-1} for the 239 cm^{-1} peak. These widths are much larger than those of previous reports.[19, 20] This might be attributed to a lattice imperfection related to Fe vacancies in the polycrystallites of β-$FeSi_2$ because of the low temperature growth and no annealing. The surface mobility of deposited species depends on the substrate temperature. Thus the lattice perfection of β-$FeSi_2$ crystallite is expected to be improved as the substrate temperature rises. However, both the peak position and the peak width do not depend on the substrate temperature. In addition to this, the results of an X-ray diffraction measurement showed that the crystallite diameters estimated using Scherrer's formula are not dependent on the substrate temperature. Thus the growth of β-$FeSi_2$ crystallites including the lattice perfection hardly depends on the substrate temperature. Two major factors, which determine the film growth, are the substrate temperature and the properties of the energetic species. These two factors control the mobility on the film surface and thereby determine the film properties. Therefore, in the PLD method, the energetic species have an important role to the growth of β-$FeSi_2$ crystallites, in particular the generation of β-$FeSi_2$ nuclei, compared with the substrate temperature, which is contrast to the other preparation methods where the structure of deposited films strongly depend on the substrate temperature.

4. CONCLUSION

β-$FeSi_2$ thin films were grown by pulsed

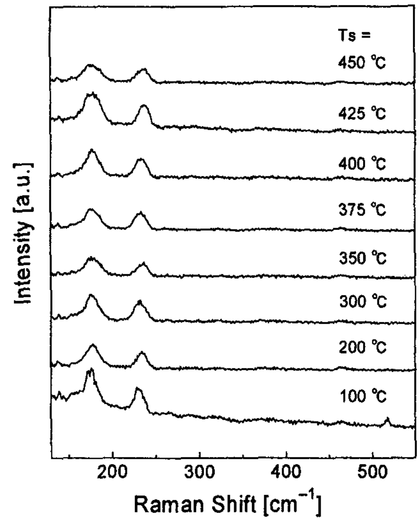

Fig. 4 Raman spectra of the films deposited at the various substrate temperature.

laser deposition (PLD) using a 193 nm laser. $FeSi_2$ alloy plate was used as the target. The films deposited using the 193 nm laser showed no droplets on the film surface at fluences between the threshold of film deposition, 2 J/cm^2 and that of droplet deposition, 4 J/cm^2. β-$FeSi_2$ thin films were prepared in this fluence range. It was found that β-$FeSi_2$ single phase films were grown at a substrate temperature between 100°C and 425°C. At the substrate temperature of more than 425°C, FeSi phase appeared in addition to the β-$FeSi_2$ phase. It is thought that the energetic species have an important role to the growth of β-$FeSi_2$ crystallites compared with the substrate temperature in PLD method. The PLD method is extremely effective to generate on the β-$FeSi_2$ film at low substrate temperature without annealing.

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