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β-$FeSi_2$ Thin Film Preparation by ECR plasma-enhanced MOCVD

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Iron silicide films were deposited on Si(100) substrates by electron cyclotron resonance(ECR) plasma enhanced MOCVD. Pentacarbonyl iron [$Fe(CO)_5$] and ferrocene [$Fe(C_5H_5)_2$] were employed as iron sources. When $Fe(CO)_5$ was used, iron deposition was ascertained at room temperature but was hardly at 550 and 900°C. On the other hand, when $Fe(C_5H_5)_2$ was used, iron deposition was ascertained at 550 and 900°C. When H_2 gas was sent to the discharge chamber for ECR plasma source, the deposition rate increased and the carbon content in the film decreased. Moreover, the carbon content was diminished by the introduction of H_2O gas into plasma together with H_2 gas and β-$FeSi_2$ films were obtained from 550 to 900°C.

Key words: β-$FeSi_2$, MOCVD, ECR-plasma

1. INTRODUCTION

Semiconducting β-$FeSi_2$ has attracted much attention over the past ten years as one of the promising materials for fabricating infrared optoelectronic devices on Si substrates. Furthermore, it is remarkable as spintronic material because iron is a constituent element. Several alternative techniques, such as ion-beam implantation (IBS)[1], reactive deposition epitaxy (RDE)[2], chemical vapor transport (CVT)[3] have been used to grow β-$FeSi_2$ thin films on silicon. However, the epitaxial β-$FeSi_2$ films growth on silicon by chemical vapor deposition (CVD) was scarcely reported. J.P.Andre *et al.*[4] deposited α-$FeSi_2$ on Si(111) from pntacarbonyl iron [$Fe(CO)_5$] and disilane (Si_2H_6) by atmospheric CVD. On the other hand, Dormans[5] and Mukaida *et al.*[6] deposited mixture of silicon carbide and iron silicide on Si(100) from ferrocene [$Fe(C_5H_5)_2$] and mono-silane (SiH_4) by atmospheric CVD.

We reported the preparation of epitaxial β-$FeSi_2$ films using $Fe(CO)_5$ and SiH_4 as precursors.[7] However, $Fe(CO)_5$ decomposed at low temperature of 150°C [8], so that the gas phase reaction prior to reaching the substrate is possible to decrease the crystalinity and the surface flatness of the film.

Another choice of Fe source is $Fe(C_5H_5)_2$ as Dormans and Mukaida *et al* reported. However, the carbon content in the film is the serious problem as they reported. In the present study, we tried to the decrease of carbon content and obtained β-$FeSi_2$ film using enhanced ion by electron cyclotron resonance (ECR) plasma enhanced metal-organic CVD (MOCVD).

2. EXPERIMENTAL

Schematic diagram of ECR-MOCVD equipment is shown in Figure 1. The cold-wall-type reactor with silicon carbide heater was used for the deposition. $Fe(C_5H_5)_2$ and $Fe(CO)_5$ were used as iron source. These were sealed in the dividual vessels and were carried to the reactor by H_2 carrier gas. On the other hand, SiH_4 was used as silicon sources. H_2 and the mixture of H_2 and H_2O gases were sent to the discharge chamber for ECR plasma source, which is designated H* ECR plasma and (H* and O*) ECR plasma, respectively. The operating pressure of the reactor was kept at $6x10^{-1}$ Pa. ECR microwave frequency was 2.45GHz. A Si (100) substrate was cleaned with 5% HF solution and rinsed in deionized water before loading into the reactor. It also *in-situ* cleaned by keeping in H_2 gas atmosphere at 1000°C for 15 min before starting the deposition.

Deposition rates of iron atom and atomic ratio of carbon to iron were estimated from the Fe *Kα* and C *Kα* to Fe *Kα* peak intensities of X-ray fluoroecence, respectively. Atomic ratio of silicon to iron in the films was measured by X-ray photoelectron spectroscopy (XPS), which was calibrated by using standard samples. The constituent phase was identified by X-ray diffraction measurement (XRD).

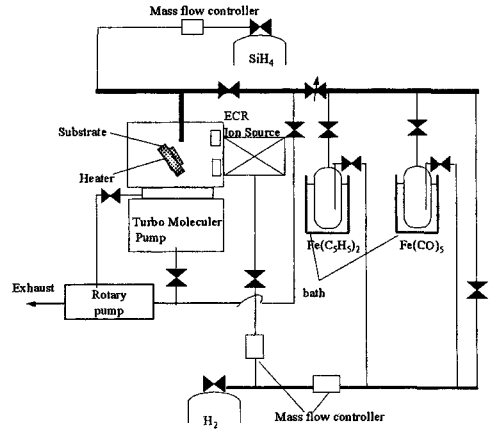

Fig.1 Schematic diagram of ECR-MOCVD equipment

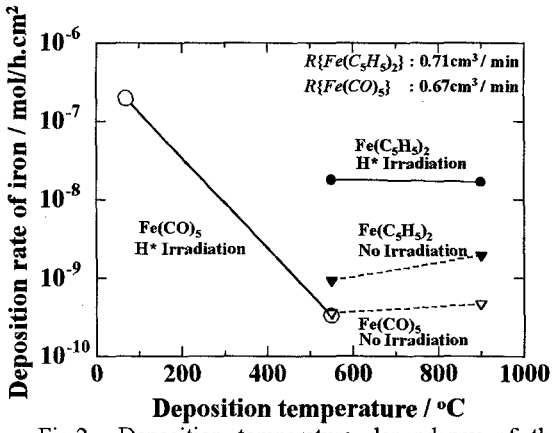

Fig.2 Deposition temperature dependency of the deposition rate of iron. (○,●) with H* ECR plasma irradiation, (▽,▼) without ECR plasma irradiation. (○ , ▽):$R\{Fe(CO)_5\}$=0.67cm³ / min, (● , ▼); $R\{Fe(C_5H_5)_2\}$=0.71cm³/ min.

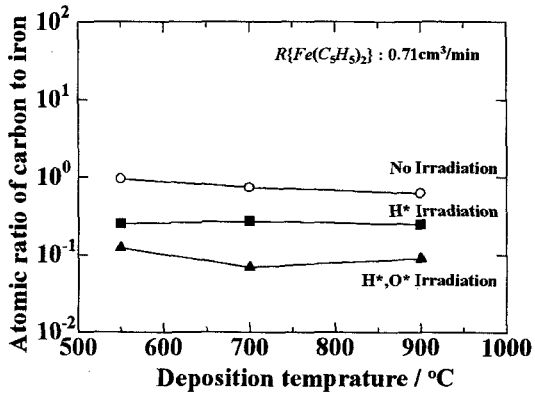

Fig3. Effect of the deposition temperature on atomic ratio of carbon to iron in the films under $R\{Fe(C_5H_5)_2\}$ of 0.71cm³/min, (○): no irradiation, (■):with H* ECR plasma irradiation, and (△): with (H* and O*) ECR plasma irradiation.

3. RESULTS AND DISCUSSION

Figure 2 shows the deposition temperature dependency of the deposition rate of iron atom. When $Fe(CO)_5$ was used as an iron source, deposition was observed at room temperature with H* ECR plasma irradiation. However, iron deposition was not observed at 550°C with H* ECR plasma irradiation. This was the same at 550°C and 900°C without H* ECR plasma irradiation. It seems to be due to the low decomposition temperature of $Fe(CO)_5$ so that $Fe(CO)_5$ is considered to be decomposed in gas phase and make powders before reaching to the substrate.

On the other hand, when $Fe(C_5H_5)_2$ was used as an iron source, the film deposition was ascertained at 550 and 900°C both of with and without H* ECR plasma irradiation. The deposition rate about 8 times increased with H* ECR plasma irradiation. In the following, $Fe(C_5H_5)_2$ was employed as an iron source to get directly crystalline β-$FeSi_2$ thin film at higher deposition temperature. Figure 3 shows the deposition temperature dependency of atomic ratio of carbon to iron on the film surface. When the film was deposited without ECR plasma irradiation, the atomic ratio of carbon to iron was high as about 1, but did not depend on the deposition temperature. It becomes to 0.25 and 0.08 with H* ECR plasma irradiation, and (H* and O*) ECR plasma irradiation, respectively. For both cases, obvious deposition temperature dependency was not observed. Reduction mechanism of carbon content with H* ECR plasma irradiation is considered to be the following reaction proposed by Dormans[5].

$$Fe(C_5H_5)_2+nH^* \Rightarrow Fe(s)+2C_5H_{5+n} \quad (n=0,1,3,5) \qquad (1)$$

Furthermore, the carbon reduction mechanism with H* and O* ECR plasma irradiation is considered to be as follows.

$$Fe(C_5H_5)_2+nH^*+2mO^* \Rightarrow Fe(s)+2C_5H_{5+n}+2mCO \quad (n=0,1,3,5)\ (m=0,1,3,5) \qquad (2)$$

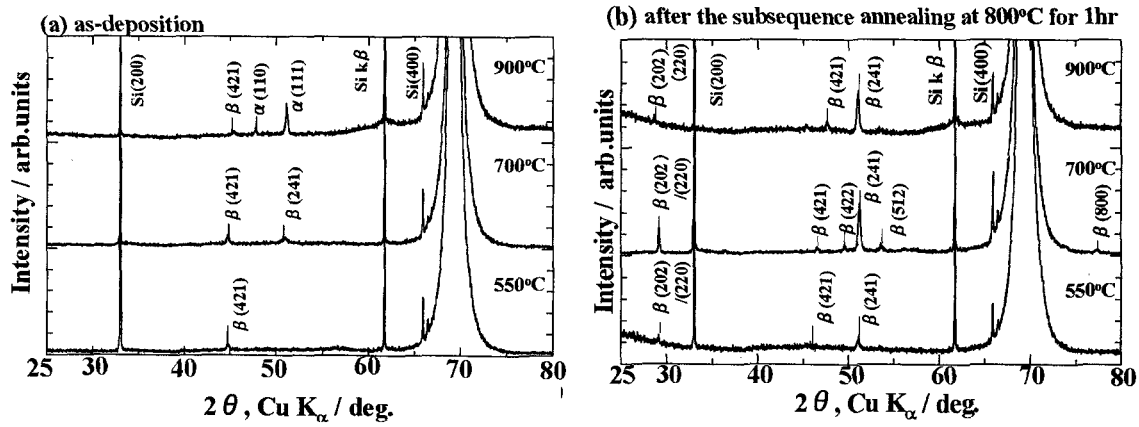

Fig.4 XRD patterns of the films deposited at various deposition temperature with (H* and O*) ECR plasma irradiation. **(a)**; as-deposition, **(b)**; after the subsequence annealing at 800°C for 1hr. Deposition temperature is indicated in figures.

Figure 4(a) shows the XRD patterns of the films deposited at various deposition temperature with (H* and O*) ECR plasma irradiation in which the atomic ratio of carbon to iron was the smallest in Figure 3. The films consisted of the single phase of β-$FeSi_2$ were deposited at 550 and 700°C even though the peak intensity was not high.

On the other hand, the film deposited at 900°C consisted of the mixture of α-$FeSi_2$ and β-$FeSi_2$. It must be pointed out that, α-$FeSi_2$ is not thermodynamically stable at 900°C in phase diagram[9]. The deposition of this thermodynamically unstable phase below 900°C was also reported by Tanaka *et al*[10].

Figure 4(b) shows the XRD patterns of the same films in Figure 4(a) after the heat treatment at 800°C in H_2 atmosphere for 1hr. The peak intensity of all films become high by this heat treatment and all films consisted of the single phase of β-$FeSi_2$. This shows that the film consisting of the single phase of β-$FeSi_2$ was obtained at the deposition temperature range of 550 to 900°C with (H* and O*) ECR plasma irradiation and the following heat treatment in H_2 atmosphere at 800°C for 1hr. However highly-oriented β-$FeSi_2$ film did not identified. At the next step, co-supply of $Fe(C_5H_5)_2$ and SiH_4 gases to the reactor was investigated.

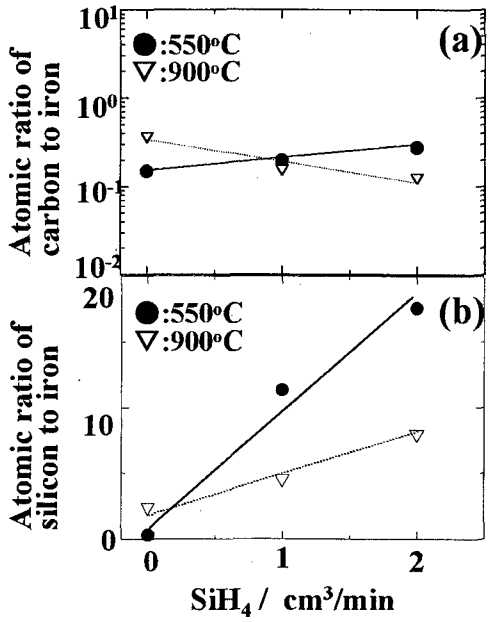

Fig.5 Effects of SiH_4 gas supply rate on atomic ratio of carbon to iron in films **(a)**, and on atomic ratio silicon to iron in films **(b)** deposited at 550°C (●) and 900°C (▽) with (H* and O*) ECR plasma irradiation.

Figure 5(a) and (b) respectively show the SiH_4 gas supply rate dependency of atomic ratio of carbon to iron and of silicon to iron in the film deposited at 550 and 900°C with (H* and O*) ECR plasma irradiation. Atomic ratio of carbon to iron was constant within the range from 0.15 to 0.3 irrespective of SiH_4 supply rate for both temperatures, as shown in Figure 5(a).

On the other hand, atomic ratio of silicon to iron increased lineally, when the SiH_4 supply rate increased as shown in Figure 5(b). It must be noticed that the atomic ratio of silicon to iron is about 2, when SiH_4 supply rate was 0 cm^3/min for the film deposited at 900°C. This is considered to the diffusion of silicon from the substrate at high temperature.

Figure 6 shows the XRD pattern change with SiH_4 supply rate for the same films as shown in Figure 5. β-$FeSi_2$ phase was ascertained to be deposited when SiH_4 supply rate was 0 cm^3/min for both temperature, even though α-$FeSi_2$ phase was coexisted at 900°C. However, the oriented film was not observed. When SiH_4 gas supply rate was above 1 cm^3/min, obvious peaks from the films were not observed, suggesting that film consisted of the amorphous phase. These films did not crystallized after the following heat treatment at 800°C under H_2 atmosphere for 1hr. It is considered to be difficult to crystalline β-$FeSi_2$ phase, because these films had silicon excess composition comparing with β-$FeSi_2$ as shown in Figure 5(b).

4.CONCLUTIONS

We succeeded in preparing β-$FeSi_2$ films on Si(100) substrates at the deposition temperature range from 550 to 900°C by ECR plasma enhanced MOCVD. The carbon content in the film decreased by H* ECR plasma irradiation and was father diminished by (H* and O*)

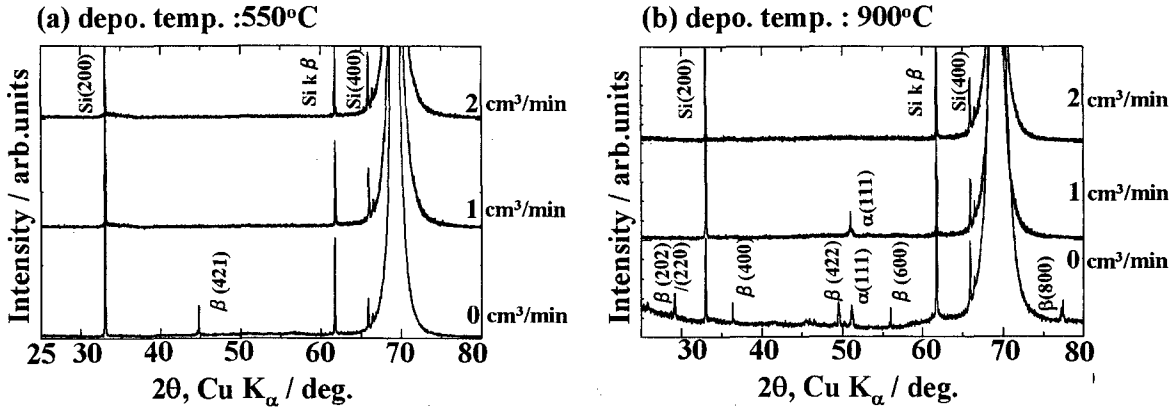

Fig.6 XRD pattern change with SiH_4 gas supply rate for the films deposited with (H* and O*) ECR plasma irradiation at 550°C **(a)**, and 900°C **(b)**. SiH_4 supply rate are indicated in figures.

ECR plasma irradiation, when $Fe(C_5H_5)_2$ was used as iron source. Deposition rate of iron increased with ECR plasma irradiation. The bond of cyclopentadienyl ligand in $Fe(C_5H_5)_2$ was broken by ECR plasma.

When $Fe(C_5H_5)_2$ and SiH_4 gases were co-supplyed, films with silicon excess composition comparing with β-$FeSi_2$ seem to be difficult to crystalline. This suggests the reaction between the film and substrate is important to get crystalline of β-$FeSi_2$ phase.

5.REFFERENCES

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