Structural, Optical and AC Conductivity Studies on Polycrystalline-Si/Nanocrystalline-FeSi$_2$ Composite Thin Films

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We investigated an electrical conduction mechanism of Si/FeSi$_2$ composite films by measuring a frequency dependence of AC electrical conductivity. The results were analyzed based upon Jonscher's power law. The hopping conduction obeying the Jonscher's power law was observed for a-Si single films after annealing as well as Si/FeSi$_2$ composite films annealed at 550 and 900°C. From the analysis of XRD, optical absorption, TEM/EDS and AC conductivity, we conclude that the electrical conduction mechanisms in polycrystalline (poly)-Si/β-FeSi$_2$ annealed at 550°C and poly-Si/α- and β-FeSi$_2$ annealed at 900°C are due to electron hopping via the conduction band of β-FeSi$_2$ and α-FeSi$_2$ nanocrystals embedded in poly-Si thin films, respectively.

1. Introduction

In recent years, a lot of research efforts in developing all-solid-state secondary battery with high safety and high capacity has been devoted and especially thin-film all-solid-state secondary batteries, which consists of an insulating layer sandwiched between two layers of p-type and n-type inorganic semiconductors, have been proposed [1, 2]. A. Nakazawa proposed a secondary battery with following structures; TiO$_2$, SnO$_2$ or ZnO as a n-type layer, NiO or CuAlO$_2$ as a p-type layer, and the charging layer filled with an n-type metal oxide semiconductors of fine particles which were coated with insulating materials [1]. Here we focus on Si/β-FeSi$_2$ composite thin films, which contain nanocrystalline β-FeSi$_2$ particles within Si matrix [3, 4]. Crystalline Si (c-Si) has an indirect band-gap ($E_g^{ind}$) of 1.12 eV [5], while the amorphous Si (a-Si) has $E_g^{ind}$ values of about 1.4-1.8 eV [6, 7]. β-FeSi$_2$ also exhibits semiconducting properties with a direct band-gap ($E_g^{dir}$) of 0.87 eV and $E_g^{ind}$ values of 0.765 eV [8, 9]. Therefore, band structure of Si/β-FeSi$_2$ composite thin films becomes similar to the charging layer of proposed secondary battery [1]. Furthermore, the difference between band gaps of Si and β-FeSi$_2$ can be arranged by the degree of crystallinity on Si. From the above points, we believe that Si/β-FeSi$_2$ composite thin films can be used as a charge layer for all-solid-state secondary battery.

However, the electrical conduction mechanism of Si/β-FeSi$_2$ composite films is still unclear. In this study, structural, optical and alternating current (AC) electrical properties of polycrystalline-Si/β-FeSi$_2$ composite thin films were evaluated and the results were compared with those of a-Si single films and the β-FeSi$_2$ single films. The electrical conduction mechanism was discussed based upon the Jonscher's law [10].

2. Experimental procedures

Three Fe chips (4N, 5×5×1 mm, Kojundo Chemical Laboratory Co., Ltd.) were arranged concentrically on a Si target (5N, φ101.6×1 mm, Kojundo Chemical Laboratory Co., Ltd.) and the
Si thin films doped with Fe atoms were deposited on the quartz substrates by RF magnetron co-sputtering (SPF-210H, CANON ANELVA Co., Ltd.) at 0.5 Pa in Ar gas (6N) atmosphere. After the deposition, these samples were annealed in an infrared lamp heating system (Mila-5000, ADVANCE RIKO, Inc.) at 550 or 900°C for 5 hours in a constant Ar gas flow rate of 100 sccm to form Si/β-FeSi₂ composite thin films. The α-Si single films and the β-FeSi₂ single films were also deposited on the quartz substrates using the Si target as described previously and FeSi₂ target (4N, φ101.6×t1 mm, Kojundo Chemical Laboratory Co., Ltd.), respectively and then they were annealed under the same above-mentioned conditions for comparison. The film thickness of all samples was around 300 nm. Finally, two rectangular-shaped Al electrodes (area: 16×6.0 mm², their distance: 4.5 mm) were deposited on these samples by vacuum thermal vaporization for AC conductivity analysis. Then these samples were alloyed at 450°C for 5 min in Ar gas to form an ohmic contact.

Structural properties of these thin films were evaluated by XRD (SmartLab, Rigaku Co., Ltd.) and TEM/EDS (H-9000NAR, Hitachi High-Technologies Co., Ltd.) analysis and their optical properties were evaluated by optical transmittance and reflectance (V-670 spectropho-meter, Jasco Co., Ltd.). Electrical characteristics of these thin films were evaluated by AC conductivity analysis (4284A LCR meter, Agilent Technologies, Inc.) at a DC bias voltage of 0 V and an AC bias voltage of either 0.05 or 1 V as a function of frequency between 100 Hz and 1 MHz.

3. Results and Discussion

Figure 1 shows XRD spectra of annealed samples: (a) FeSi₂ single films subjected to annealing at 550°C, (b) Si single films subjected to annealing at 550°C, (c) Si/FeSi₂ composite films subjected to annealing at 550°C, and (d) Si/FeSi₂ composite films subjected to annealing at 900°C. It was found from Fig. 1(a) that FeSi₂ single films subjected to annealing at 550°C shows a polycrystalline β-FeSi₂ structure. XRD spectrum of (b) Si single films subjected to annealing at 550°C exhibit an amorphous Si structure, while that of (c) Si/FeSi₂ composite films subjected to annealing at 550°C consists of polycrystalline Si and polycrystalline β-FeSi₂. The cause of formation of polycrystalline Si at low temperature of 550°C is considered to be due to the metal induced crystallization (MIC) [11, 12]. It should be noted that (d) Si/FeSi₂ composite films subjected to annealing at 900°C consist of metallic α-FeSi₂, semiconducting β-FeSi₂ and poly-Si. We estimated the crystallite sizes, D of poly-Si for samples (c) and (d) by Scherrer’s equation \( k=0.9 \) [13] using the F.W.H.M. values of Si (311) peaks in Figs. 1 (c) and 1 (d), and they were determined to be 3.5 and 7.5 nm, respectively.

![Fig. 1. XRD spectra of annealed samples](image-url)
Figures 2 (a) and 2 (b) show TEM images of the poly-Si/β-FeSi$_2$ and poly-Si/α- and β-FeSi$_2$ composite thin films formed by annealing at 550 and 900°C, respectively. From the TEM/EDS analysis, the black dots and grey area were identified as FeSi$_2$ and Si, respectively. The particle sizes of FeSi$_2$ dot crystals shown in Figs. 2 (a) and 2(b) were estimated using ImageJ (an open source image processing program) to be 6.8 and 18.8 nm, respectively. Similarly, the distances between FeSi$_2$ particles shown in Figs. 2 (a) and 2(b) were estimated to be 8.95 and 19.5 nm, respectively.

Figure 3 shows optical absorption spectra of annealed samples, which were derived from optical transmittance and reflectance measurements. It is reasonable that the optical absorption coefficient of (d) poly-Si/α- and β-FeSi$_2$ composite films is much smaller than that of (c) poly-Si/β-FeSi$_2$ composite thin films because the reflectance increases with increasing the amount of metallic α-FeSi$_2$.

Optical indirect and direct band-gap values ($E_{g\text{ ind}}$ and $E_{g\text{ dir}}$) for β-FeSi$_2$ and Si were determined from the optical absorption spectra using Tauc relation [14]. They were $E_{g\text{ dir}}$=0.74 eV for β-FeSi$_2$ single films, $E_{g\text{ ind}}$=1.51 eV for α-Si single films, $E_{g\text{ ind}}/E_{g\text{ dir}}$=1.24/0.88 eV for poly-Si/β-FeSi$_2$ composite films, and $E_{g\text{ ind}}/E_{g\text{ dir}}$=1.08/0.96 eV for poly-Si/α- and β-FeSi$_2$ composite films. It is known that the band-gap of Si decreases with increasing the degree of crystallinity of Si [15]. As mentioned above, crystallite sizes of poly-Si for poly-Si/β-FeSi$_2$ composite films annealed at 550°C and poly-Si/α- and β-FeSi$_2$ composite films annealed at 900°C were determined to be 3.5 and 7.5 nm, respectively.

The difference of the degree of crystallinity is one of the possible origin of the difference of $E_{g\text{ ind}}$ for poly-Si. On the other hand, $E_{g\text{ dir}}$ for β-FeSi$_2$ depends on chemical composition of Fe/Si as well as the degree of crystallinity of β-FeSi$_2$. The reason for difference in $E_{g\text{ dir}}$ for β-FeSi$_2$ is currently unclear. Further investigation on chemical composition of Fe/Si for β-FeSi$_2$ nanocrystals is needed.

The summary of analysis results from TEM images and optical absorption spectra is listed in Table I.

![Fig. 2. TEM images of poly-Si/β-FeSi$_2$ films formed by annealing at 550°C (a) and poly-Si/α- and β-FeSi$_2$ films formed by annealing at 900°C (b).](image)

![Fig. 3. Optical absorption spectra of annealed samples: (a) β-FeSi$_2$ single films subjected to annealing at 550°C, (b) α-Si single films subjected to annealing at 550°C, (c) poly-Si/β-FeSi$_2$ films formed by annealing at 550°C, and (d) poly-Si/α- and β-FeSi$_2$ films formed by annealing at 900°C.](image)
Table 1. Summary of analysis results from TEM images and optical absorption spectra

| Sample              | The particle size of FeSi$_2$ [nm] | The distance between FeSi$_2$ particles [nm] | Optical band gap [eV] |
|---------------------|------------------------------------|----------------------------------------------|-----------------------|
| a-Si 550°C          | -                                  | -                                            | 1.51                  |
| β-FeSi$_2$ 550°C    | -                                  | -                                            | 0.74                  |
| poly-Si/β-FeSi$_2$ 550°C | 6.8                               | 8.9                                          | 1.24 / 0.87           |
| poly-Si/α- and β-FeSi$_2$ 900°C | 18.8                              | 19.5                                         | 1.08 / 0.96           |

Figure 4(a) shows the angular frequency dependence of the electrical AC conductivity for various films after annealing. It is known that the AC electrical conductivity of a substance exhibiting hopping conduction obeys Jonscher's power law and it is expressed as Eq. (1) [10, 16, 17],

\[
\sigma_{ac} = A \omega^s, \quad \omega = 2\pi f \quad (1)
\]

where \(A\) is a constant dependent on temperature, \(\omega\) is the angular frequency, \(f\) is frequency and \(s\) is the frequency exponent \((0 < s \leq 1)\). Hopping conduction was observed for three types of films; a-Si single films after annealing at 550°C, poly-Si/β-FeSi$_2$ composite films formed by annealing at 550°C and poly-Si/α- and β-FeSi$_2$ composite films formed by annealing at 900°C. It has been suggested that the electric conduction mechanism of amorphous materials is mainly due to hopping conduction [18, 19]. Therefore, it is natural that a-Si single films after annealing show hopping conduction in a wide range of angular frequency. On the other hand, poly-Si/β-FeSi$_2$ and poly-Si/α- and β-FeSi$_2$ composite films show hopping conduction only at higher angular frequencies and in a wide range of angular frequency, respectively. The discussion of these electrical conduction mechanisms will be described later.

The polaron binding energy, \(W_m\) and the lower bound cut off to hopping distance, \(R_{min}\) were calculated using Eqs. (2) [16] and (3) [17], respectively,

\[
s = 1 - \frac{6kT}{W_m} \quad (2)
\]

\[
R_{min} = \frac{n e^2}{\pi \epsilon \epsilon_0 W_m} \quad (3)
\]

where \(k\) is the Boltzmann constant, \(T\) is the temperature, \(n=1, 2\) for single and bi-polarons, \(\epsilon\) is the elementary charge, and \(\epsilon \epsilon_0\) is the relative dielectric constant of a material and dielectric constant of a vacuum, respectively. Here, the value of \(\epsilon\) was calculated from the capacitance value of each sample, which was measured by AC conductivity analysis as a function of frequency. The values of \(R_{min}\) were obtained assuming \(n=2\) and they are shown in Fig. 4(b) as a function of angular frequency. Curve fitting results using Eqs. (1)-(3) are summarized in Table II.

The difference between bottom of conduction bands of crystalline-Si (electron affinity, \(\chi = 4.05\) eV) [20] and β-FeSi$_2$ (\(\chi = 4.71\) eV) [20] can be estimated to be 0.66 eV, which almost agrees well with \(W_m\) value (0.64 eV) of poly-Si/β-FeSi$_2$ composite films. In addition, as shown in Table I, the distance between FeSi$_2$ particles for poly-Si/β-FeSi$_2$ composite films was 8.9 nm, which is of the same order of magnitude as \(R_{min}\) value (3.3 nm) of poly-Si/β-FeSi$_2$ composite films. For the above reasons, it is suggested that the electrical conduction in poly-Si/β-FeSi$_2$ composite films is due to electron hopping via the conduction band of β-FeSi$_2$. Similarly, the difference between bottom of conduction bands of crystalline-Si (\(\chi = 4.05\) eV) [20] and α-FeSi$_2$ (work function=5.3-5.5 eV) [21]
can be estimated to be 1.43-1.45 eV, which is roughly close to $W_m$ value (1.88 eV) of poly-Si/α- and β-FeSi$_2$ composite films. Work function of 5.3-5.5 eV on α-FeSi$_2$ is larger than electron affinity of 4.71 eV on β-FeSi$_2$. Therefore, it is suggested that the electrical conduction in poly-Si/α- and β-FeSi$_2$ composite films is due to electron hopping via the conduction band of α-FeSi$_2$. The distance between FeSi$_2$ particles for poly-Si/α- and β-FeSi$_2$ composite films was 19.5 nm, which is of the different order of magnitude as $R_{min}$ value (2.3 nm) of poly-Si/α- and β-FeSi$_2$ composite films. This reason is currently unclear because poly-Si/α- and β-FeSi$_2$ composite films consist of mixed phase of α- and β-FeSi$_2$. We need to form and evaluate poly-Si/α-FeSi$_2$ single phase composite films to clarify it.

Table II. Summary of AC conductivity analysis

| Sample                  | annealing | $s$ | $W_m$ [eV] | $R_{min}$ [nm] |
|-------------------------|-----------|-----|------------|----------------|
| a-Si single films       | 550°C     | 1.00| $\infty$  | N/A            |
| Si/FeSi$_2$ composite   | films     | 0.762 | 0.64      | 3.3            |
| films                   | 900°C     | 0.909 | 1.88      | 2.3            |

4. Conclusion

XRD and optical absorption spectra of β-FeSi$_2$ single films showed a polycrystalline β-FeSi$_2$ structure with the $E_g^{\text{dir}}$ value of 0.74 eV, while those of a-Si single films exhibited an amorphous Si structure with the $E_g^{\text{ind}}$ value of 1.51 eV. We found that the poly-Si/β-FeSi$_2$ composite films annealed at 550°C consist of polycrystalline Si ($E_g^{\text{ind}} = 1.24$ eV) and nanocrystalline β-FeSi$_2$ ($E_g^{\text{dir}} = 0.87$ eV, the particle size is 6.8 nm). Similarly, we found that the poly-Si/α- and β-FeSi$_2$ annealed at 900°C composite films consist of nanocrystalline α-FeSi$_2$ and β-FeSi$_2$ ($E_g^{\text{dir}} = 0.96$ eV, the particle size is 18.8 nm) and polycrystalline Si ($E_g^{\text{ind}} = 1.08$ eV).

We investigated an electrical conduction mechanism of Si/FeSi$_2$ composite films by measuring a frequency dependence of AC electrical conductivity. The results were analyzed based upon Jonscher’s power law and the three parameters, $s$, $W_m$ and $R_{min}$ were determined by fitting the calculated values to the experimental data. The hopping conduction obeying the Jonscher’s power law was observed for a-Si single films after annealing as well as Si/FeSi$_2$ composite films annealed at 550 and 900°C. The hopping conduction in a-Si films has been reported so far. From the result of comparison between $W_m$ values and the band diagram of Si/FeSi$_2$ as well as between $R_{min}$ values and the distance between FeSi$_2$ particles, we conclude that the electrical conduction mechanisms in poly-
Si/β-FeSi₂ and poly-Si/α- and β-FeSi₂ composite films are due to electron hopping via the conduction band of β-FeSi₂ and α-FeSi₂ nanocrystals embedded in poly-Si films, respectively.

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