Interface-state density estimation of n-type nanocrystalline FeSi₂/p-type Si heterojunctions fabricated by pulsed laser deposition*

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Abstract
By utilizing pulsed laser deposition (PLD), heterojunctions comprised of n-type nanocrystalline (NC) FeSi₂ thin films and p-type Si substrates were fabricated at room temperature in this study. Both dark and illuminated current density–voltage (J–V) curves for the heterojunctions were measured and analyzed at room temperature. The heterojunctions demonstrated a large reverse leakage current as well as a weak near-infrared light response. Based on the analysis of the dark forward J–V curves, at the V value ≤ 0.2 V, we show that a carrier recombination process was governed at the heterojunction interface. When the V value was > 0.2 V, the probable mechanism of carrier transportation was a space-charge limited-current process. Both the measurement and analysis for capacitance–voltage–frequency (C–V–f) and conductance–voltage–frequency (G–V–f) curves were performed in the applied frequency (f) range of 50 kHz–2 MHz at room temperature. From the C–V–f and G–V–f curves, the density of interface states (Nsi) for the heterojunctions was computed by using the Hill–Coleman method. The Nsi values were 9.19 × 10¹² eV⁻¹ cm⁻² at 2 MHz and 3.15 × 10¹⁴ eV⁻¹ cm⁻² at 50 kHz, which proved the existence of interface states at the heterojunction interface. These interface states are the probable cause of the degraded electrical performance in the heterojunctions.

Keywords: NC-FeSi₂/Si heterojunctions, J–V curve, C–V–f curve, G–V–f curve, interface state

Classification numbers: 2.07, 4.10, 5.01, 5.03

1. Introduction
Several researchers have reported that semiconducting iron disilicide (β-FeSi₂) comprising nontoxic elements (Si and Fe) has attracted much attention recently as a new promising candidate for application in silicon-based optoelectronic devices [1–4]. It is because β-FeSi₂ possesses both indirect and direct optical bandgaps of 0.74 eV, and 0.85 eV, respectively. These optical bandgap values are of relevance to optical fiber telecommunication wavelengths [5–7]. Additionally, β-FeSi₂ grown epitaxially on Si with small lattice mismatches [8–10] has an optical absorption coefficient of more than 10⁵ cm⁻¹ at 1.2 eV [11–13]. Nanocrystalline (NC) FeSi₂ grown on any solid substrate at room temperature possesses semiconducting features close to β-FeSi₂ [14–16]. It is comprised of a crystal with diameter range of 3–5 nm [17] and has a larger
The distance of the substrate to the FeSi$_2$ target was fixed at 193 nm was focused onto the rotating FeSi$_2$ target using a 50 mm. An argon-fluorine (ArF) laser beam with a wavelength of 193 nm was used for PLD by utilizing a FeSi$_2$ target. The oxide layer was initially removed from the substrate by utilizing hydrofluoric acid (HF) and then cleaned with deionized water. The cleaned substrate was instantly mounted on a substrate holder in a PLD chamber. The PLD chamber had a base pressure of 10$^{-6}$ torr.

### 2. Experimental details

NC-FeSi$_2$ thin films with a thickness of 100 nm were grown on a p-type Si(1 1 1) substrate at room temperature by means of PLD by utilizing a FeSi$_2$ target. The oxide layer was initially removed from the substrate by utilizing hydrofluoric acid (HF) and then cleaned with deionized water. The cleaned substrate was instantly mounted on a substrate holder in a PLD chamber. The PLD chamber had a base pressure of 10$^{-6}$ torr. The distance of the substrate to the FeSi$_2$ target was fixed at 50 mm. An argon-fluorine (ArF) laser beam with a wavelength of 193 nm was focused onto the rotating FeSi$_2$ target using a spherical lens. The repetition rate of the laser pulses was 10 Hz and fluence was 10 J cm$^{-2}$. A radio frequency magnetron sputtering apparatus was used to form the back and front ohmic contacts of the heterojunctions. Pd films were formed on the back of the Si in a finger-shaped pattern, whereas Al films were formed on the whole NC-FeSi$_2$. A schematic diagram of the n-type NC-FeSi$_2$/p-type Si heterojunctions fabricated utilizing PLD is shown in figure 1.

The crystalline structure for the NC-FeSi$_2$ thin films grown on Si substrate was characterized by utilizing x-ray diffraction (XRD; Rigaku RINT2000/PC). Observation of the surface morphology of the NC-FeSi$_2$ thin films grown by PLD was performed by using the Carl Zeiss Auriga field emission scanning electron microscope (FESEM) at Facility Building 10 (F10), the Center for Scientific and Technological Equipment, Suranaree University of Technology. The NC-FeSi$_2$ thin films grown by PLD were also observed by transmission electron microscopy (TEM; JEM-2000EX Conventional TEM) at the Ultramicroscopy Research Center, Kyushu University [17]. The measurement of the current density–voltage ($J$–$V$) curves for the heterojunctions was performed by utilizing a Keithley 2400 source meter at room temperature in the dark.

In a previous study, NC-FeSi$_2$ thin films were investigated for their structural and electrical features [17]. The NC-FeSi$_2$ thin films possessed n-type conduction and a carrier density ranging between 10$^{18}$ to 10$^{19}$ cm$^{-3}$ [17]. After that, the near-infrared (NIR) light detection performance for the n-type NC-FeSi$_2$/p-type Si heterojunctions fabricated utilizing PLD was studied [14]. Based on the experimental results, the fabricated heterojunctions demonstrated a large reverse leakage current and a weak NIR light response at room temperature. A probable cause was likely the existing interface states at the heterojunction interface between NC-FeSi$_2$ and Si have not been studied in detail yet.

In the present study, the measurement and analysis of capacitance–voltage–frequency ($C$–$V$–$f$) and conductance–voltage–frequency ($G$–$V$–$f$) curves of the n-type NC-FeSi$_2$/p-type Si heterojunctions fabricated utilizing PLD were performed at room temperature. The $N_{ss}$ value at the heterojunction interface between NC-FeSi$_2$ and Si was computed by utilizing the Hill–Coleman method. It proved the existence of interface states for the heterojunctions in this study. These interface states probably are the cause of the degraded electrical properties in the aforementioned heterojunctions. Additionally, the probable transportation mechanism of the carrier through the heterojunction interface was studied. At $V \leq 0.2$ V, the predominant transportation mechanism of the carriers was the recombination process. It was governed by a space-charge-limited current (SCLC) process at $V > 0.2$ V. According to the available knowledge of the authors, this study is the first investigation of the $N_{ss}$ value and probable transportation mechanisms of the carrier at room temperature for the n-type NC-FeSi$_2$/p-type Si heterojunctions fabricated utilizing PLD.

Figure 1. Schematic diagram for n-type NC-FeSi$_2$/p-type Si heterojunctions fabricated utilizing PLD.

Figure 2. XRD patterns for NC-FeSi$_2$ film deposited by PLD and FTDCS (for comparison), which were measured by utilizing a grazing incidence method (2θ scan) at a fixed incidence angle of 4°, on the back of the Si in a finger-shaped pattern, whereas Al films were formed on the whole NC-FeSi$_2$. A schematic diagram of the n-type NC-FeSi$_2$/p-type Si heterojunctions formed utilizing PLD is shown in figure 1.

The crystalline structure for the NC-FeSi$_2$ thin films grown on Si substrate was characterized by utilizing x-ray diffraction (XRD; Rigaku RINT2000/PC). Observation of the surface morphology of the NC-FeSi$_2$ thin films grown by PLD was performed by using the Carl Zeiss Auriga field emission scanning electron microscope (FESEM) at Facility Building 10 (F10), the Center for Scientific and Technological Equipment, Suranaree University of Technology. The NC-FeSi$_2$ thin films grown by PLD were also observed by transmission electron microscopy (TEM; JEM-2000EX Conventional TEM) at the Ultramicroscopy Research Center, Kyushu University [17]. The measurement of the current density–voltage ($J$–$V$) curves for the heterojunctions was performed by utilizing a Keithley 2400 source meter at room temperature in the dark and under the illumination of a 6 mW of 1.31 µm laser diode. The measurements of $C$–$V$–$f$ and $G$–$V$–$f$ curves were carried out with an LCR meter (Agilent E4980A) at room temperature with the $f$ value range of 50 kHz–2 MHz. From the $C$–$V$–$f$ and $G$–$V$–$f$ curves, the series resistance ($R_s$) value was computed...
by utilizing the Nicollian–Brews method and the $N_{vo}$ value was computed by utilizing the Hill–Coleman method.

3. Results and discussion

The typical XRD patterns of the NC-FeSi$_2$ film deposited on a Si(1 1 1) substrate by PLD and Si(1 1 1) substrate (background) are shown in figure 2. The measurement was performed utilizing a grazing incidence method ($2\theta$ scan) at a fixed incidence angle of $4^\circ$. For comparison, the XRD pattern of the NC-FeSi$_2$ film, which resulted from the overlapping of broad peak is likely owing to the nanocrystalline structure such as 331, 313, 040, 004, 041, 114, 511, 422, and 133. Thus, the broad peak is likely owing to the nanocrystalline structure of the NC-FeSi$_2$ film, which resulted from the overlapping of diffraction peaks for these crystalline planes [14, 15, 17]. Due to the robust quenching of highly-energetic species on the surface of the substrate, the nucleation of FeSi$_2$ immediately takes place in the PLD process. Nanocrystallites comprising the NC-FeSi$_2$ film should be nuclei formed in the mentioned process [14]. The broad peak of NC-FeSi$_2$ film deposited by PLD is weak compared with that of NC-FeSi$_2$ film deposited by FTDCS [15]. In this range, orthorhombic FeSi$_2$ has several crystalline planes for diffraction, such as 331, 313, 040, 004, 041, 114, 511, 422, and 133. Thus, the broad peak is likely owing to the nanocrystalline structure of the NC-FeSi$_2$ film, which resulted from the overlapping of diffraction peaks for these crystalline planes [14, 15, 17].

Figure 3(a) shows a FESEM image of the NC-FeSi$_2$ thin films grown by PLD. From the obtained FESEM image, the NC-FeSi$_2$ thin films have a very smooth surface and consist of numerous crystallites with diameters of 4–5 nm. Figure 3(b) displays the dark-field image of NC-FeSi$_2$ thin films using the broad ring [17]. The NC-FeSi$_2$ thin films consist of a large number of small crystallites with diameters ranging from 3 to 5 nm. This result corresponds to the FESEM image.

Figure 4 demonstrates the room temperature $J$–$V$ curves of n-type NC-FeSi$_2$/p-type Si heterojunctions under reverse and forward bias voltage conditions, in the dark and under illumination of a 6 mW, 1.31 $\mu$m laser light. The heterojunctions demonstrated a rectifying action similar to that observed in conventional pn abrupt junctions. However, the heterojunctions demonstrated a large reverse leakage current. In addition, the illuminated current under reverse bias voltage increased slightly compared with that of dark current. These results were probably because of the existing interface states at the heterojunction interface between NC-FeSi$_2$ and Si acting as a center of leakage current and a trap center for the photogenerated carriers [14–16].

The study of the dark forward $J$–$V$ curve demonstrated the probable transportation mechanisms of the carrier via the ideality factor ($n$). Figure 5 shows the dark forward $J$–$V$ curve for n-type NC-FeSi$_2$/p-type Si heterojunctions. The current increases with a $V$ value and it shows a downward curvature at high $V$ value. At the $V$ value $\leq$ 0.2 V, the $J$ value shows a linear change with the $V$ value. This could be explained utilizing the diode equation as follows [20–23]:

$$J = J_0 \exp \left(\frac{qV}{nkT}\right) - 1,$$

(1)

where $J$, $J_0$, $T$, $V$, $k$, and $q$ are the current density, diode saturation current density, absolute temperature, applied bias voltage, Boltzmann’s constant, the electron charge and ideality factor, respectively. From equation (1), the $n$ value was computed from the slope of the linear part of the forward $\ln J$–$V$ curve through the following relationship:

$$n = \frac{q}{kT} \frac{dV}{d(\ln J)} = \frac{q}{kT} \text{slope}.$$

(2)

Fundamentally, the predominant transportation mechanism of the carriers is a diffusion process if the value of $n$ is $n = 1$, while the predominant transportation mechanism is a carrier recombination process if the $n$ value is $> 1$ and $\leq 2$. If the $n$ value is $> 2$, the predominant transportation mechanism of carrier is a tunneling process.

From the computation by using equation (2), the $n$ value was 1.73. The implication is that the predominant transportation mechanism at the heterojunction interface between the NC-FeSi$_2$ and Si was a carrier recombination process. The
existing defects in NC-FeSi₂ thin films might generate the deep energy levels in the bandgap. These energy levels could act as a center for recombination.

In the range of \( V > 0.2 \) V, the \( V \) value was sufficient to provide the carriers with sufficient energy to overcome the potential barrier at the junction. Thus, the concentration of the charge was insignificant when compared to that of the injected charges. This shows that space-charge recombination takes place and controls the transportation of the carrier [24]. In essence, if the SCLC process dominates the transportation of the carrier, the \( J \) value displays a power-law dependence of the \( V \) value as follows: \( J \propto V^m \). Here, the parameter \( m \) was higher than 2. The inset in figure 5 is a plot of \( \log J - \log V \) for the heterojunctions. This plot shows a linear fit between \( \log J \) and \( \log V \) in the range of \( V > 0.2 \) V. The parameter \( m \) computed from the slope of straight line was 2.32. The value of \( m \geq 2 \) suggests that the transportation of carrier was governed by the SCLC in this bias voltage range [25, 26].

Figure 6(a) displays the \( C-V-f \) curves for the heterojunctions. The measurements performed at room temperature in the \( f \) value range of 50 kHz–2 MHz showed from the curves, that the \( C \) value decreased when the \( f \) value was increased. The \( G-V-f \) curves for the heterojunctions are displayed in figure 6(b). It was clear that the \( G \) value increased when the \( f \) value was increased.

The \( R_s \) and \( N_{ss} \) values are vital parameters for the electrical characteristics of the heterojunctions. The Nicollian–Brews method is appropriate to compute the \( R_s \) value and expressed as [27–29]:

\[
R_s = \frac{G_m}{G_m^2 + (\omega C_m)^2}.
\]

Here, the \( G_m \) and \( C_m \) values are the conductance and capacitance in strong accumulation region, respectively, and \( \omega \) is angular frequency.

The Hill–Coleman method was employed to compute the \( N_{ss} \) value. According to this method, the value of \( N_{ss} \) was computed from the measured \( C-V-f \) and \( G-V-f \) curves by utilizing the following relationship [28, 29]:

\[
N_{ss} = \frac{2}{qA} \frac{(G_m/\omega)_{\text{max}}}{((G_m/\omega)_{\text{max}}C_m)^2 + (1 - C_m/C_{ox})^2},
\]

where \((G_m/\omega)_{\text{max}}\) and \(C_m\) are the conductance and capacitance corresponding to the maximum values, \(A\) is the heterojunction area, and \(C_{ox}\) is the insulator oxide layer capacitance and can be expressed as:

\[
C_{ox} = C_m \left[1 + \frac{G_m^2}{(\omega C_m)^2}\right].
\]

The \( R_s-V-f \) curves for the heterojunctions are displayed in figure 7. It was found that the \( R_s \) value decreased when the \( f \) value was increased. This is likely because the charges at the interface states could not follow the ac signal when the \( f \) value was high [27–29]. The \( N_{ss}-f \) curves for the heterojunctions are illustrated in figure 8. From computation by using equation (4), the \( N_{ss} \) values were \( 3.15 \times 10^{14} \) eV\(^{-1}\) cm\(^{-2}\) at 50 kHz and \( 9.19 \times 10^{12} \) eV\(^{-1}\) cm\(^{-2}\) at 2 MHz. This proved the existence of interface states at the heterojunction interface between NC-FeSi₂ and Si. These interface states acted as the center of leakage current and trap center for photo-generated carriers and thus degraded the electrical properties of the heterojunctions. In addition, it was observed that the value of \( N_{ss} \) decreased exponentially when the \( f \) value was increased. In the region of the low \( f \) values \((f \leq 300\) kHz\)), the value of \( N_{ss} \) strongly depended on the \( f \) value, causing increasing of the \( C \) value in the n-type NC-FeSi₂/p-type Si heterojunctions. The high \( C \) values at low \( f \) values were likely owing to the excess \( C \) value resulting from the \( N_{ss} \), which was in equilibrium with the semiconductor following the ac signal [30–32]. In contrast, the value of \( N_{ss} \) was almost independent of the \( f \) value at \( f > 300\) kHz. Normally, the interface states are in equilibrium with the semiconductor and do not contribute to the \( C \) value at sufficiently high \( f \) values because the charge at the interface states cannot follow the ac signal [32].

Additionally, the carrier density for the grown NC-FeSi₂ thin films utilizing PLD is approximately \( 10^{19}\) cm\(^{-3}\). This large
A Nopparuchikun et al. 5 carrier density value is expected to degrade the light detection of the fabricated n-type NC-FeSi2/p-type Si heterojunctions due to narrowing of the depletion region that expands into the NC-FeSi2 layer. Hence, the large carrier density of the grown NC-FeSi2 thin films should be further suppressed.

4. Conclusions

n-Type NC-FeSi2/p-type Si heterojunctions were fabricated by utilizing PLD at room temperature. The fabricated heterojunctions demonstrated a large reverse leakage current as well as a small NIR light response. According to the analysis of the dark forward J–V curves, a recombination process was governed at \( V \leq 0.2 \) V, while a SCLC process was governed at \( V > 0.2 \) V. From the computation of the \( N_{ss} \) values by utilizing the Hill-Coleman method, the \( N_{ss} \) values were \( 3.15 \times 10^{14} \) eV\(^{-1}\) cm\(^{-2}\) at 50 kHz and \( 9.19 \times 10^{12} \) eV\(^{-1}\) cm\(^{-2}\) at 2 MHz. This proved the existence of interface states at the heterojunction interface between NC-FeSi2 and Si. These interface states acted as the center for leakage current as well as a trap center for photo-generated carriers, which was the likely cause for the degraded electrical performance of the heterojunctions at room temperature.

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