RAPID COMMUNICATION

Resonant energy transfer from nanocrystal Si to β-$FeSi_2$ in hybrid Si/β-$FeSi_2$ film*

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The photoluminescence (PL) characteristics of hybrid β-$FeSi_2$/Si and pure β-$FeSi_2$ films fabricated by pulsed laser deposition at 20 K are investigated. The intensity of the 1.54-μm PL from the former is enhanced, but the enhancement vanishes when the excitation wavelength is larger than the widened band gap of Si nanocrystal. Time-resolved PL decay measurements reveal that the lifetime of the photo-excited carriers in the hybrid β-$FeSi_2$/Si film is longer than that in the pure β-$FeSi_2$ film, providing evidence that the PL enhancement results from the resonant charge transfer from nanocrystalline Si to β-$FeSi_2$.

Keywords: β-$FeSi_2$ nanocrystal, photoluminescence, resonant charge transfer

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1. Introduction

Beta-phase iron silicide (β-$FeSi_2$) is an environmentally friendly semiconductor possessing many unique physical and chemical properties such as high resistance to oxidation and corrosion as well as strong light absorption. It also exhibits photoluminescence (PL) at 1.54 μm which is a transmission window of optical silica fibers.[1] These advantages render β-$FeSi_2$ a promising candidate in near infrared detectors, light emitters, solar cells, and other applications.[2–4] Many techniques have been adopted to produce nanosized β-$FeSi_2$ materials, for instance, ion beam synthesis, reactive epitaxy, magnetron sputtering, pulsed-laser deposition, and molecular beam epitaxy, and their PL properties have also been explored.[5–9] It has been pointed out that the origin of the PL from β-$FeSi_2$ is quite complicated because of the controversial band gap structure. Most experiments have suggested that β-$FeSi_2$ has a direct band gap,[1,4–6] but some reports have indicated otherwise.[10–12] The 1.54-μm PL has been assigned to the band-to-band recombination of β-$FeSi_2$ or dislocation defects in the Si substrate.[13,14] In the strained β-$FeSi_2$/Si system, the band gap of β-$FeSi_2$ transforms from indirect to direct due to strain making the 1.54-μm PL a feature of direct recombination. Meanwhile, this also suggests that Si may play an important role in the PL from β-$FeSi_2$.

Resonant charge transfer is a common effect in the interdot interaction in the nanocrystal (NC) ensemble.[15–17] In the β-$FeSi_2$/Si system, Si NCs are excellent donors and can improve the PL from nanoscale β-$FeSi_2$ (acceptors) due to the absorption and emission spectral overlap.[18] In the present work, Si and β-$FeSi_2$NCs are deposited on Si (100) substrates and pronounced enhancement is observed from the 1.54-μm PL from the β-$FeSi_2$NCs. This enhancement is attributed to resonant charge transfer from nanoscale Si to β-$FeSi_2$.

2. Samples and experiments

Sample deposition was carried out via pulsed laser deposition in a conventional pulsed laser deposition configuration consisting of a femtosecond laser system, a vacuum chamber, and a β-$FeSi_2$ and Si hybrid target (β-$FeSi_2$ and Si each account for wt 50%), p-type (100) silicon (3 Ω·cm–8 Ω·cm) substrates. The distance between the target and substrate was fixed to be 50 mm. The laser source used was a KrF excimer laser (248 nm) with an energy density of about 1.2 J/cm^2. During the deposition, the base pressure in the chamber was maintained to be less than 4×10^{-5} Pa and the temperature of the substrates was maintained at 600 °C. The deposition time for the hybrid β-$FeSi_2$/Si film sample was 75 min (about 500-nm thick). For comparison, individual β-$FeSi_2$ and Si targets were also used to deposit pure β-$FeSi_2$ and Si NC films under the same conditions, the deposition times were 100 min and 50 min, respectively (controlled with 500-nm thick). The three deposited samples were annealed in an Ar atmosphere at 1100 °C for 2 h and then kept at 900 °C for 12 h. The annealed hybrid β-$FeSi_2$/Si, pure β-$FeSi_2$, and pure nc-Si films were

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denoted as samples 1, 2, and 3, respectively. The sample structure was determined on an M03XHF22 X-ray diffractometer (XRD) with Cu K_α radiation under grazing incidence geometry and a Jobin Yvon T64000 triple Raman system with the 514.5-nm line of an Ar^+ laser serving as an excitation source. The PL spectra were obtained by an Edinburgh FLS-920 PL spectrometer equipped with an infrared detector. Three continuous excitation sources at 325-, 632-, 1050-nm lines from three lasers were used. All the measurements were conducted at 20 K unless otherwise stated.

3. Results and discussion

Figure 1 shows the Raman spectra and XRD patterns of the three samples. The XRD diffraction and Raman peaks of samples 2 and 3 can be assigned to β-$FeSi_2$ and nanocrystalline Si (nc-Si), respectively. However, both the XRD pattern and Raman spectrum of sample 1 show the β-$FeSi_2$ and nc-Si signals. Accordingly, it can be inferred that samples 2 and 3 are pure β-$FeSi_2$ and nc-Si films, whereas sample 1 is a hybrid film including both β-$FeSi_2$ and nc-Si. In each of the spectra acquired from the hybrid β-$FeSi_2$/Si and nc-Si film (samples 1 and 3), there is a strong broad XRD peak at about $2\theta = 28^\circ$, suggesting that the crystal size of the nc-Si is $D_c = 0.89\lambda/(B\cos\theta) = \sim 3.1$ nm according to calculation based on the Scherrer formula. The diffraction peaks from the β-$FeSi_2$ (sample 2) are sharper and the crystal size is determined to be about 65 nm. Transmission electron microscopy (TEM) confirms that the size is in a range from 50 nm to 80 nm (data not shown here). Here, it should be pointed out that such small Si NCs in sample 3 do not show a noticeable asymmetric Raman peak at 500 cm^{-1}–521 cm^{-1} and only a strong peak is observed at 521 cm^{-1}. This is due to large background scattering of the silicon substrate, which conceals the asymmetric broadening of the 521-cm^{-1} Raman peak caused by the small Si NCs.

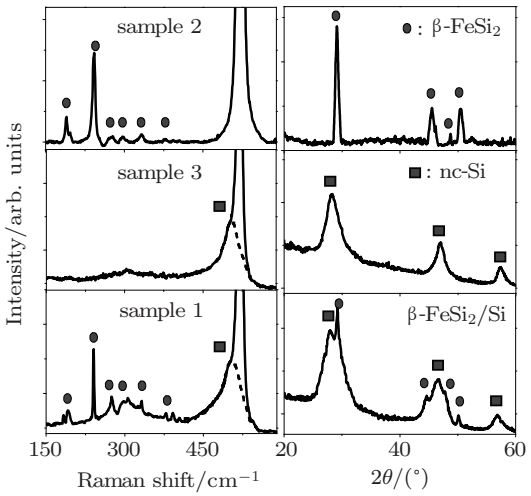


Fig. 1. XRD patterns and Raman spectra acquired from the pure β-$FeSi_2$ film (sample 2), pure nc-Si film (sample 3), and hybrid β-$FeSi_2$/Si film (sample 1).

Figure 2(a) depicts the PL spectra of the three samples in a wavelength range between 700 nm and 1650 nm at 20 K. The pure nc-Si and hybrid β-$FeSi_2$/Si films show PL peaks at about 885 nm (1.40 eV) and 880 nm (1.41 eV), respectively. These peaks are associated with the Si NCs. According to the quantum confinement effect, in small NCs, the band gap energy can be described as[19]

$$E_g^{\text{eff}} = E_g^{\text{bulk}} + \frac{\hbar^2\pi^2}{2\mu R^2} - \frac{1.8e^2}{\varepsilon R},$$

where E_g^{eff} is the band gap of the Si NCs, E_g^{bulk} is the band gap of bulk Si, R is the NC radius, μ is the effective mass, and ε is static dielectric constant. Based on an Si NC size of 3.1 nm, the broadened band gap of the Si NCs is about 1.4 eV, which is in good agreement with the experimental PL peak position, indicating that the high energy PL peak arises from quantum confinement in the Si NCs. Here, it should also be mentioned that the formation of the quantum confinement on Si NCs is due to the existence of Si oxide in the film, which can be seen in the high diffraction background of the XRD pattern in the low-angle diffraction side in Fig. 1 (sample 1). In the low-energy region, the pure β-$FeSi_2$ film (sample 2) shows a relatively weak PL peak at 1.54 μm, which corresponds to the band–band recombination of β-$FeSi_2$. This intensity of this peak observed from the hybrid β-$FeSi_2$/Si film is increased by a factor of 2. The result is quite interesting because sample 2 has more β-$FeSi_2$ compositions than sample 1 and should have a more intense PL peak, contrary to our experimental observation. This implies that a resonant charge transfer process may occur between the NC Si and β-$FeSi_2$.[20] It should be pointed out that the β-$FeSi_2$/Si film shows a weak shoulder peak at 1.45 μm, which is associated with defects in the Si substrate.[13,16] These Si defects may not exist in all Si substrates such as those with the nc-Si film here.

To investigate the resonant charge transfer process, PL spectra are acquired from the hybrid β-$FeSi_2$/Si film under excitation by three wavelengths of 325, 632, and 1050 nm but at the same power. As shown in Fig. 3, the intensity of the 1.54-μm PL peak from the β-$FeSi_2$/Si film increases initially as the excitation wavelength is increased from 325 nm to 632 nm, but decreases as the excitation wavelength is changed to 1050 nm (upper inset). For comparison, the PL intensity observed from the pure β-$FeSi_2$ film shows a steady increase as the excitation wavelength is increased from 325 nm to 632 nm and then 1050 nm (lower inset). Figure 2(a) shows that the emission from the Si NCs is at about 880 nm and that the quantum-confined band gap is about 1.4 eV (880 nm). Under the excitation of 1050-nm light, Si NCs with a band gap of 880 nm cannot be excited nor can the resonant charge transfer from Si to β-$FeSi_2$ occur. Hence, the PL intensity diminishes. In addition, no resonant charge transfer occurs in defect states in the Si substrate to β-$FeSi_2$ because the 1.45-μm PL intensity

observed from defects in the Si substrate hardly changes when the excitation wavelength is varied.

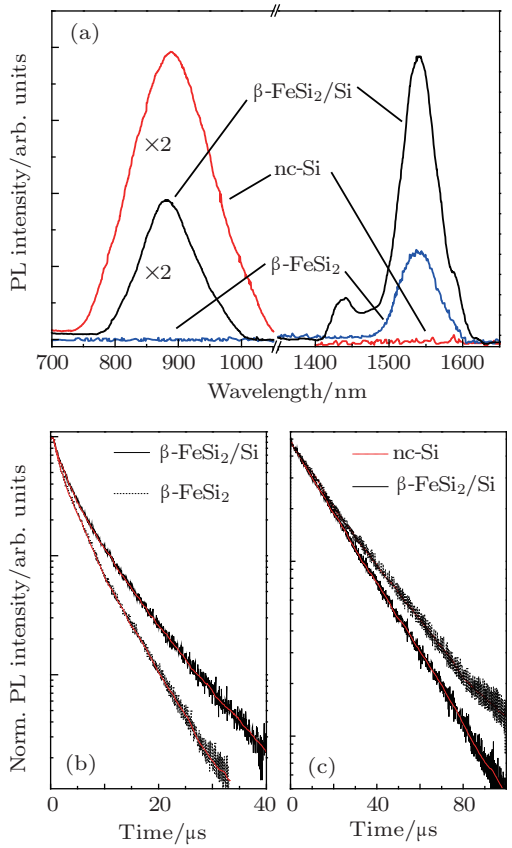


Fig. 2. (color online) (a) Steady-state PL spectra of the pure β-$FeSi_2$ film, hybrid β-$FeSi_2$/Si film, and pure nc-Si film. (b) Time-resolved PL decay curves of the pure β-$FeSi_2$ and hybrid β-$FeSi_2$/Si films monitored at 1.54 μm. (c) Time-resolved PL decay curves of the pure nc-Si and hybrid β-$FeSi_2$/Si films monitored at 880 nm. All the spectra are obtained at $T = 20$ K.

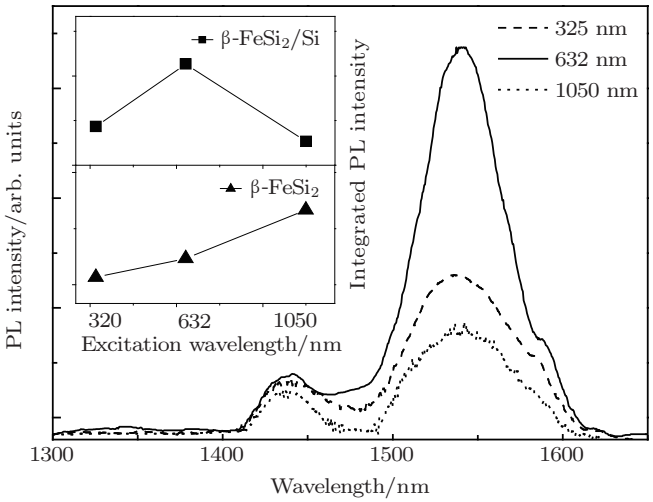


Fig. 3. PL spectra ($T = 20$ K) of the hybrid β-$FeSi_2$/Si film acquired under excitations of the 325 (dashed line), 632 (solid line), and 1050 nm (dotted line) lines of three different lasers. The insets show the relationship between the PL intensity and excitation wavelength for the hybrid β-$FeSi_2$/Si and pure β-$FeSi_2$ films.

Resonant charge transfer is often accompanied by an increase in donor lifetime. To determine the mechanism, the time-resolved PL decay curves of the luminescence yield at 1.54 μm of the hybrid β-$FeSi_2$/Si and pure β-$FeSi_2$ films are displayed in Fig. 2(b). The decay curves are the sum of two exponentials as shown in the following:[21]

$$I(t) = I_{\text{fast}} \exp(-t/\tau_{\text{fast}}) + I_{\text{slow}} \exp(-t/\tau_{\text{slow}}),$$

where I_{fast} and I_{slow} are the PL intensities of the components with decay times of I_{fast} and I_{slow}, respectively. The experimental curve of the hybrid β-$FeSi_2$/Si film is reproduced using τ_{fast} and τ_{slow} parameters of 8 ns and 12 μs, respectively. With regard to the pure β-$FeSi_2$ film, there are fast and slow decay times of about 10 ns and 8 μs, respectively. The slow decay time of the hybrid β-$FeSi_2$/Si film is longer than that of the pure β-$FeSi_2$ film. The ratio of the PL intensity I_{slow} to I_{fast} calculated from the pure β-$FeSi_2$ film is 1.5 and this value reaches 4 in the hybrid β-$FeSi_2$/Si film. This indicates that the slow decay components are dominant in the hybrid β-$FeSi_2$/Si film. The fast decay is generally ascribed to band-to-band recombination in the β-$FeSi_2$ with direct gap, but the slow decay curves are more controversial. The latter have been attributed to a defect-related transition in Si[21,22] or indirect transition of the β-$FeSi_2$.[23,24] Our experimental results reveal no Si-related defect luminescence at $\sim$ 1.54 μm (Fig. 2(a)) and the observed PL at 1.54 μm is more intense when the excitation line is close to the emission band of the Si NCs (Fig. 3). Considering that the size of the β-$FeSi_2$NCs is about 65 nm, we believe that the transformation from indirect to direct gap by strain is difficult. Since the 1.54-μm PL has an energy corresponding to the band gap of bulk β-$FeSi_2$ and our experiment data show that the slow decay component is dominant in the transition, a new process, namely resonant charge transfer, should be involved in the 1.54-μm PL from the hybrid β-$FeSi_2$/Si film.

Figure 2(c) shows the time-resolved PL decay curves of the 880-nm emission acquired from the pure nc-Si and hybrid β-$FeSi_2$/Si films. The two decay curves can be fitted by a single exponential relationship of $I(t) = I\exp(-t/\tau)$, and the decay times are calculated to be 11 μs for the pure nc-Si film and 7.6 μs for the hybrid film. The former is larger than the latter, which is opposite to that observed from the 1.54-μm PL decay times calculated from the pure and hybrid β-$FeSi_2$ films. This phenomenon can be explained by resonant charge transfer from Si NCs to β-$FeSi_2$. According to the charge transfer channel,[16] the dynamics of Si NCs in the hybrid β-$FeSi_2$/Si film can be described by the following rate equation

$$1/\tau_{\text{hybrid}} = 1/\tau_{\text{pure}} + \Gamma_{\text{transfer}},$$

where $1/\tau_{\text{hybrid}}$ and $1/\tau_{\text{pur}}$ are the PL decay rates of the Si NCs in the hybrid β-$FeSi_2$/Si and pure nc-Si films, respectively, and Γ_{transfer} is the charge transfer rate. The charge transfer efficiency can be written approximately as[16]

$$E = \frac{\Gamma_{\text{transfer}}}{1/\tau_{\text{hybrid}}}.$$

Here, factors such as the Auger and back-transfer processes are ignored. According to this equation, the charge transfer efficiency in the hybrid β-$FeSi_2$/Si film is determined to be about 32%. Figure 4 shows the schematic diagram of the resonant charge transfer process taking place in the hybrid β-$FeSi_2$/Si film. The Si NC has a higher conduction band and a lower valence band than β-$FeSi_2$ and so under large power laser irradiation, a large number of charges and holes are produced. They are transferred to the conduction band and valence band of the β-$FeSi_2$, respectively, to produce radiative recombination, thereby leading to the enhanced 1.54-μm PL observed from the hybrid film.

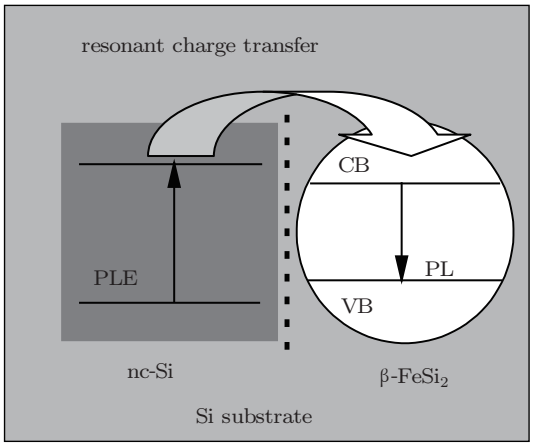


Fig. 4. Schematic illustration of the resonant charge transfer process between the Si NCs and β-$FeSi_2$ in the hybrid β-$FeSi_2$/Si film.

4. Conclusions

The enhanced PL at 1.54 μm is observed from the hybrid β-$FeSi_2$/Si film. Spectral analysis suggests that the nc-Si improves the luminescence efficiency of the band-to-band recombination in the β-$FeSi_2$ and the resonant charge transfer from the Si NCs to β-$FeSi_2$/Si leads to the enhanced emission.

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