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Growth of β-$FeSi_2$ Nanocrystals by Phase Transition and Enhancement of Light Emission Property

Kentaro Nishimura[1], Takahito Nakajima[1], Yoshiyuki Nagasawa[1], Kazumasa Narumi[2], and Yoshihito Maeda[1,2]

[1] Graduate School of Energy Science, Kyoto University
Sakyo-ku, Kyoto 606-8501, Japan
Phone: +81-75-753-4722 E-mail: maeda@energy.kyoto-u.ac.jp
[2] Advanced Science Research Center, Japan Atomic Energy Agency
Tokai, Ibaraki 319-1195, Japan

1. Introduction

Semiconducting β-$FeSi_2$ (β-phase) with an orthorhombic structure has been noteworthy about an infrared (IR) light emitting material at telecommunication wavelengths [1, 2], light absorbing layers at IR part in the solar spectrum [3], antireflection coatings [4], photonic crystals [5-7] and light emitters such as LEDs [2, 8]. However, present light emitting efficiency is not sufficient for infrared light emitting devices. Many efforts have been done in order to improve the efficiency by decreasing interfacial defects and stacking faults which are attributed to a large lattice mismatch (1.5-4%) and differences in crystal structures or growth rates between the β-phase and Si [2, 5, 8-12].

γ-$FeSi_2$ (γ-phase) is a metastable phase with a fluorite structure and a metallic conduction property [1]. Theoretical studies have revealed that the origin of β-phase formation with semiconductive property can be attributed to a Jahn-Tellar type distortion of the γ-phase lattice. Above 600°C the γ-phase transforms into the equilibrium β-phase. The γ-phase has almost the same lattice constant as Si has, and lattice mismatch at the heterointerface is very small, so that epitaxial growth of the γ-phase on Si proceeds. It should be noted that the epitaxial relationships between Si and the γ-and β-phases, Si(111)//γ(111)// β(202),(220), can be maintained even after the phase transition taking place above 600°C [13]. On the other hand, direct precipitation of β-phase by a silicidation reaction, $Fe+Si_2=FeSi_2$ [1], may little maintain such an epitaxy because of homogeneous nucleation and thermally accelerated growth in Si.

We have focused attention on those epitaxial relationships which have inspired us a distinguished method for enhancement of the light emission from the nanocrystals with better coherent or less defective interfaces with Si(111). Such an idea can be realized by following crystallographic steps, the first step is precipitation of the γ-phase on Si(111), the second one is a phase transition from the γ-phase into the β-phase.

In this study, we have systematically investigated photoluminescence properties of the β-phase nanocrystals formed by controlling the phase transition from the γ-phase.

2. Experiments

The β-$FeSi_2$ nanocrystal precipitated in a Si crystal matrix were prepared by ion-beam synthesis (IBS) containing both processes of $^{56}Fe^+$ ion implantation (the energy of 200keV, the dose of 10^{17} ions/cm^2) and the subsequent annealing [5,10,11]. A profile of the subsequent annealing of samples contains a double thermal annealing process [14] both at 500°C (preannealing) and at 800°C (postannealing).

Photoluminescence (PL) was excited with an Ar^+ ion laser at 514.5nm and the PL spectrum was measured with a monochromator and a liquid N_2 cooled Ge pin photodiode.

3 Results and Discussion

PL spectra with sharp peaks at 0.803eV measured at 8.3K are shown in Fig.1. The PL spectrum showed a clear response by changing in the preannealing time. In Fig.1(a), the peak intensity corresponding to the intrinsic A band of the β-phase was surely enhanced by the preannealing in comparison with the case in Fig.1(c) without the preannealing. However, in Fig.1(b) the peak intensity slightly decreased. This result is very important and teaches us that only the preannealing dose not dominates the PL enhancement and how long time of postannealing is necessary for PL enhancement observed in Fig.1(a).

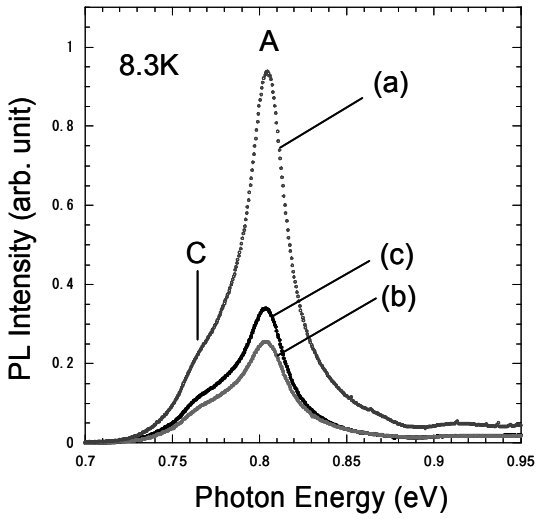

Fig. 1 PL spectra measured at 8.3K from β-$FeSi_2$ nanocrystals formed by annealing either at (a) 500°C for 8h and 800°C for 6h, (b) 500°C for 8h and 800°C for 2h, or (c) 800°C for 2h. The symbol A means the A band of intrinsic emission from β-$FeSi_2$, and C means an emission band due to a band to impurity transition [5].

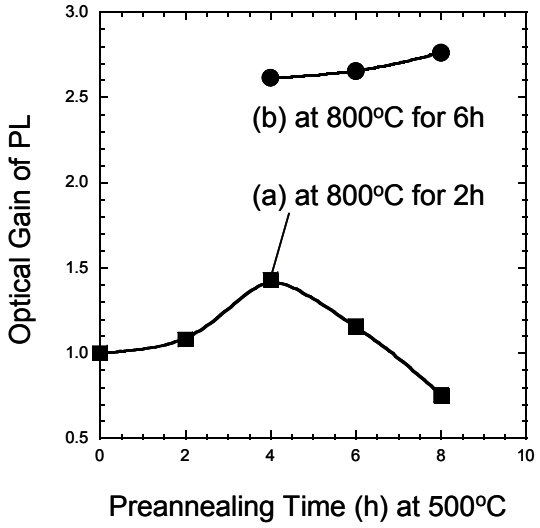

Fig. 2 Optical gain of the A band intensity in comparison with the case without preannealing (only with annealing at 800°C for 2h) for each case of postannealing at 800°C for (a) 2h (previous data [14]) and (b) 6h.

Figure 2 shows an optical gain of the A band peak intensity as a function of the preannealing time at 500°C. We also examined an effect of the postannealing time for 2h (previous data [14]) and 6h at 800°C. In the results, we observed pronounced PL enhancement with the maximum gains up to 280% in the case of Fig.1(b). The preannealing time at 500°C surely controls amount of the γ-phase precipitated on Si(111), and the postannealing time at 800°C dominates final amount of the β-phase nanocrystals with coherent interfaces as well as the γ→β phase transition. The best case for PL enhancement may be that all the γ-phase formed during the preannealing completely transforms into the β-phase after the postannealing for suitable time. The cases of 8h in Fig.1(b) surely correspond to such an optimum cases.

We would discuss the possible mechanism of the PL enhancement observed in this study. In general, dependence of the PL efficiency (I_{PL}) on the excitation power (P) by a pumping laser on is very helpful to understand the emission mechanism. It has been reported that the intrinsic A band emission from the β-phase nanocrystal directly precipitated at 800°C has a power low between I_{PL} and P (I_{PL}~P^m). In a low pumping rate, the exponent *m* is close to one, while in the high rate m is close to 0.5 [11]. The nanocrystals with large optical gains had the same power dependence as the usual nanocrystals have. This suggests that no special change of the radiative recombination process takes place in the nanocrystal formed through the phase transition.

Next we examined phonon properties of the nanocrystal because the radiative recombination at the indirect band-gap of β-$FeSi_2$ needs emission of suitable phonon at low temperature. The typical four infrared absorption peaks relating to LO or TO phonons (at 328-323, 358, and 438 cm^{-1}) are characteristic for phonon states in the β-$FeSi_2$ nanocrystals [15]. Except for small differences in the absorption peaks at 328-323 cm^{-1}, we observed no clear differences in the IR spectra between the nanocrystal formed through the γ→β phase transition and the nanocrystal precipitated directly by annealing at 800°C.

Interface states between the nanocrystal and Si are also considerable as origin of non-radiative recombination centers [10]. In the annealing process employed in this study, the nanocrystal via the γ-phase can be expected to grow epitaxially on Si(111) because the epitaxial relationship, β(202),(220)//γ(111)//Si(111) can be maintained even after the phase transition [13]. This inspires us that such a tight crystallographic correlation among the phases may realize the least defective interface between the nanocrystal and Si(111) and the least defective interface leads to the pronounced enhancement of PL intensity observed in Figs. 1 and 2.

4. Conclusions

We have succeeded in enhancement of the PL intensity by using a double thermal annealing process, in which the β-phase nanocrystal formed by the phase transition between the γ and β-phases. It is speculated that the PL enhancement observed may be attributed to improvement of the interface condition (the least defective interface) between the nanocrystal and Si(111).

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