Light Emission from β-$FeSi_2$

Yoshihito Maeda[1,2]

[1] *Department of Computer Science and Electronics, Kyushu Institute of Technology, Iizuka, Fukuoka 820-8502, Japan*
[2] *Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1110, Japan*
Phone: +81-948-29-7653 E-mail: maeda@cse.kyutech. ac.jp

ABSTACT

Orthorhombic β-$FeSi_2$ is one of a few semiconductors which can be applied to IR-light emitters at optical telecom at 1.55-1.3 μm of wavelength. Actual situation of its light emission is not close to realization of practical uses in optoelectronics, however, efficiency of rad-$FeSi_2$ iative recombination has been uplifted by controlling crystal growth and by fabricating nanometer-sized structures (nanostructures).

My lecture in ICSS-Silicide 2014 is based on our group's researches on IR-light emission from a hetero-system of β-$FeSi_2$ and Si and aims at giving the whole phenomena relating to light emission from β-$FeSi_2$ in order to draw a true picture for understanding it as much as possible. **We emphasize** important facts that IR radiative processes are strongly dependent upon micro-structures of crystalline units for radiative recombination. In this meaning, nano-composite phases consisting of β-$FeSi_2$ nanocrystals are appropriate to light emitters.

This lecture contains the following topics.

Contents of lectures (tentative)

1. Research Background
1.1 Gre*en technology* toward sustainable optical telecom technology
- 1.1.1 What are problems in optical telecom technology? (*see* Figure 1)
- 1.1.2 Why do we need β-$FeSi_2$?
- 1.1.2 What is light emission from β-$FeSi_2$
- 1.1.3 How do we do the crystal growth?

2. Light emission observed in some crystal phases
2.1 PL behaviors dependent upon growth or synthesis methods
- 2.1.1 High purity synthesis of crystals by ion-beam technology
- 2.1.2 Film deposition methods
- 2.1.3 Bulk crystals

2.2 Understanding of emission bands observed in PL spectra
- 2.2.1 Intrinsic A band emission (*see* Figure 2)
- 2.2.2 Impurity-related C band emission (*see* Figure 2)
- 2.2.3 Defects-related bands emission (*see* Figure 3)

3. Photoluminescence properties of nano-composite phases
3.1 β-$FeSi_2$/Si nano-composite phases
- 3.1.1 Microstructure observations
- 3.1.2 Band structures

3.2 A band emission
- 3.2.1 Temperature and pumping dependences
- 3.2.2 Time resolved measurements
- 3.2.3 Photo-carrier injection PL measurements (*see* Figures 5-8)

3.3 Impurity related emission
- 3.2.1 Temperature and pumping dependences
- 3.2.2 Related impurity levels

4. Enhancement of PL
4.1 Impurity doping
- 4.1.1 Al doping
- 4.1.2 Cu doping (*see* Figures 4-8)

4.2 γ->β phase transition
4.3 Oxidation (*see* Figure 9)

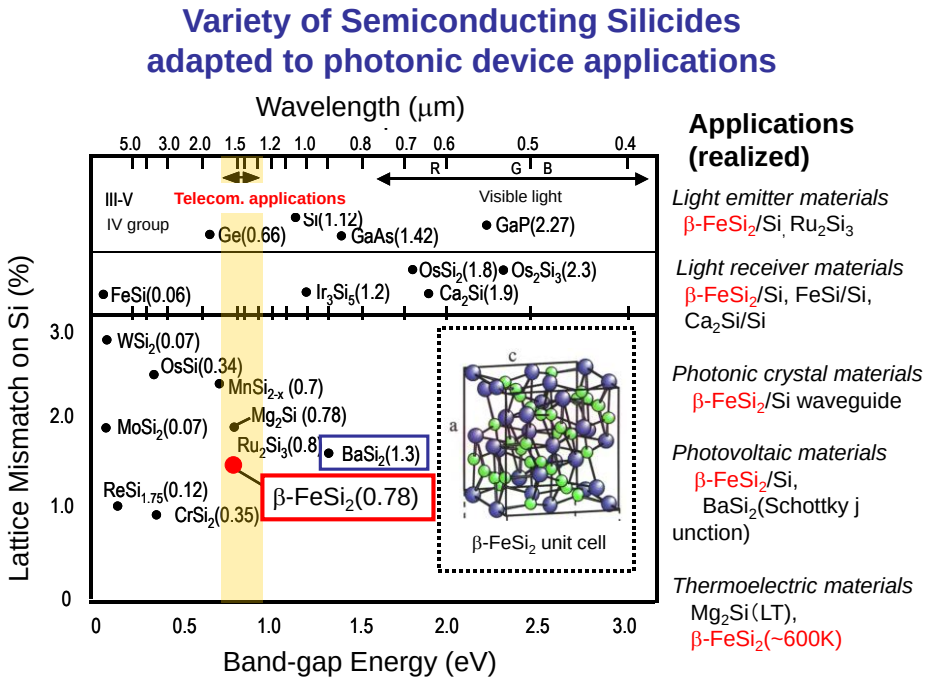
5. Future study required moreover

5.1 Further enhancement of radiative recombination rate
5.2 Thermal quenching (damping) problem (*see* Figure 9)

6. Conclusions

Some key figures and their explanations

1. Research Background



Y. Maeda and Y. Terai：Bull. Inst. of Metals Japan, MATERIA 2005 Jun.

Figure 1

Semiconducting silicides that are available to applications optoelectronics, photonics, photovoltaics and thermoelectronics on Si platforms. Their band-gaps (or band-gap wavelengths) and lattice mismatch ratios on the Si substrate are crucial parameters for applications to telecom technology. Orthorhombic $FeSi_2$ (β-$FeSi_2$), cubic Mg_2Si, $MnSi_{2-x}$, and Ru_2Si_3 have their band-gap wavelengths near the telecom wavelength. Radiative processes of IR light have been confirmed in β-$FeSi_2$, and reported in Ru_2Si_3. $BaSi_2$ with the band-gap of 1.3 eV as been studied in order to apply it high efficient solar cells.

(*Cited from* Y. Maeda and Y. Terai, Article published in Bulletin of Japan Inst. Metals, Jun vol. 2005)

2. Light emission observed in some crystal phases

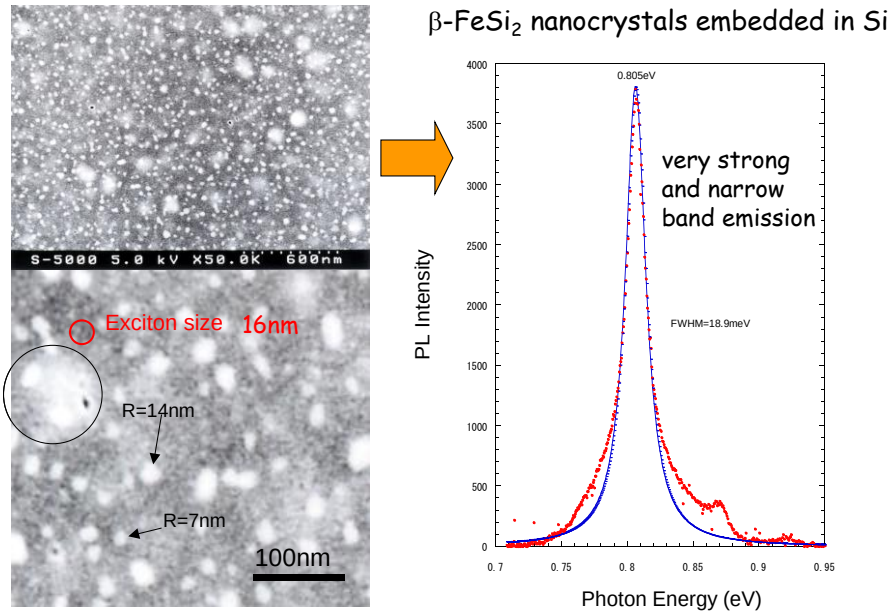


Figure 2

A typical photoluminescence (PL) spectrum with an intrinsic emission due to the radiative indirect transition in β-$FeSi_2$ (A band emission) and the impurity (or defect)-related emission (C band emission). This PL spectrum mainly consists of the A band emission with a Lorentz function shape and the C band emission weakly appears at its shoulder. This observation tells us the important fact that the correct or pure observation of the radiative process in β-$FeSi_2$ can be only in the nano-composite phase as shown in the left figure). The nanocrystals size is same to or less than the effective Bohr size of 16 nm of Mott-Wannier type excitons in β-$FeSi_2$. This structural evidence teaches us that the migration of the M-W type excitons in the crystal is limited (exciton confinement). This confinement contributes enhancement of a radiative recombination rate of electrons-holes. This better electronic situation due to exciton confinement realized in the nano-composite phase leads high efficient radiative recombination at the A band emission. The C band emission at ~0.77 eV at 8 K is originated from impurity-band transitions. In the case of non-doped samples the origin of impurity level (band) is silicon atomic vacancy (V_{Si}) in the β-lattice, in the case of impurity doped samples acceptor or donor levels are formed. It has been observed that the C band intensity is dependence upon an impurity doping dose. In Cu-doping case, enhancement of the C band emission depending on the Cu doping dose was clearly observed. (*see* Fig4)

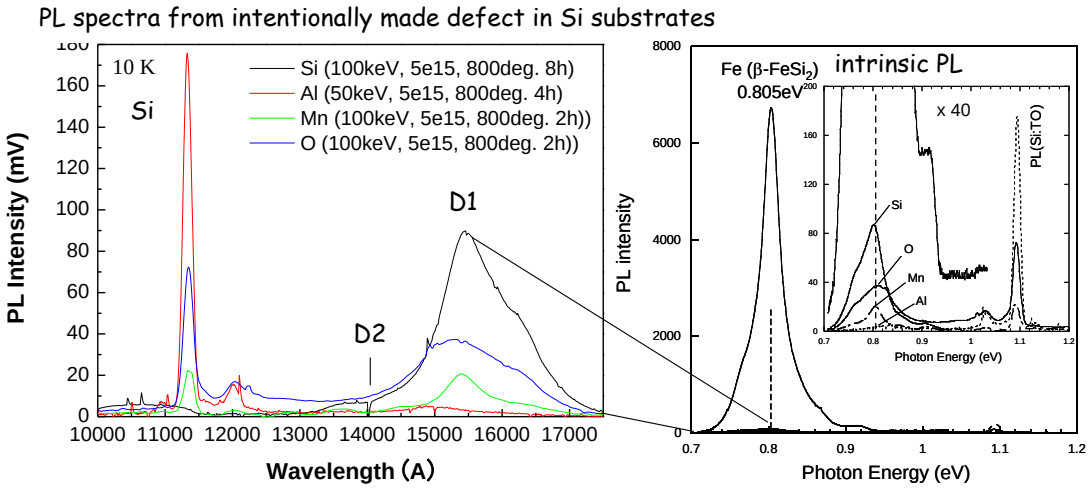


Figure 3

Some PL spectra observed from Si substrates implanted by some ions with high energies and high doses. In these ion implantation gives damages into implantation depth of Si substrates. In the damaged region, atomic vacancy, interstitial atoms and higher ordered crystal defects such as dislocations (DL), looped DLs. It has been reported that one of these defects, especially lopped DLs, can emit IR light, unfortunately, the emission energy of the D1 line (the strongest DL-related emission line) at ~1550 nm (~0.81-0.82eV) is very close to that of intrinsic A band emission. However, this situation about IR light emission may be more complicated than that estimated by us. The left spectra show this complicated situation well, and very broad emission bands but their peak energies and intensities are different each other. These similarity between such a defect-related PL (DRPL) and the intrinsic A band PL have made chaos for understanding nature of light emission from β-$FeSi_2$ itself. Compering the defect-related PL spectrum and the intrinsic A band emission as shown in the right figure, we found that the DRPL intensity was much smaller than the A band one as shown in an inset of the right figure. This means that the DRPL intensity may be proportional to the implanted dose under the competition with nonradiative processes brought by the implantation at the same time. In general, the density of LDs and their density of state (DOS) as a radiative unit may be much smaller than a joint density of state (JDOS) at interband transition. These big differences in the JDOS and DOS between them are reason of observed difference in the PL intensities. (*cited from* Y. Maeda, Appl. Surf. Sci., **254** (2008) 6242.)

3. Photoluminescence properties of nano-composite phases

4. Enhancement of PL

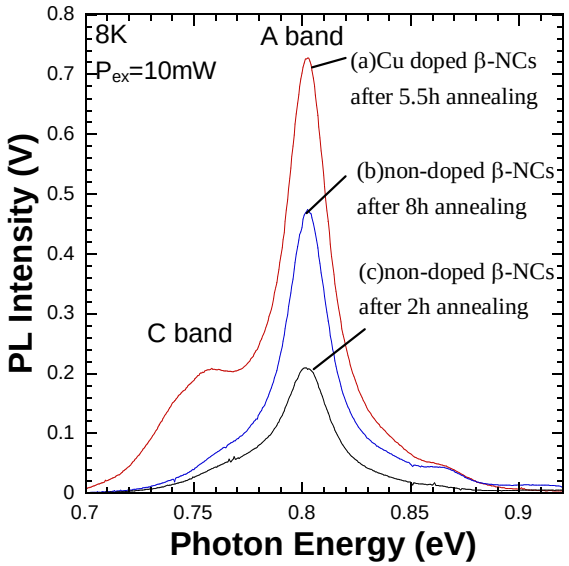


Figure 4

PL spectra of Cu-doped β-$FeSi_2$/Si nano-composited phase thermally treated for different time. The thermal treatment time corresponds to doping dose of Cu into the nano-composite phase. We found that Cu causes pronounced enhancement of both the A band and the C band emissions. The C band emission enhancement can be understood by increase of the DOS at the acceptor level due to Cu^+ activated in the β-lattice. However, the enhancement of the A band emission at 0.803 eV at 8 K cannot be understood by the same reason. One of the possible reasons is improvement of heterointerfaces between β-$FeSi_2$ and Si by Cu-doping. TEM observations revealed that semi-coherent interfaces can be realized in Cu-doped β-$FeSi_2$/Si heterointerfaces. However, in the β-$FeSi_2$ nanocrystals (β-NCs)

such a coherent interface with Si can be realized because the β-NC size is very small (~10 nm in size) and total lattice mismatch is small (less than the critical length for generation of screw dislocations). The Mott-Wannier (M-W) type exciton generated in β-NCs has a large effective Bohr radius (a_B=~8 nm) because of the large static dielectric constant (ε_0) of β-$FeSi_2$. In the β-NCs of less than ~10 nm in size, the M-W excitons can be confined well if the band-offsets at the conduction and valence bands between β-$FeSi_2$ and Si. Photocurrent measurements have made it evident that the band-off energy of holes (ΔE_V in Fg.5) at the β-$FeSi_2$/Si hetero-interface is too small to realize confinement of holes in the β-NCs. Therefore, a part of holes can go out from the β-NCs to the Si matrix by thermal activation. Radiative recombination rate at steady state can be controlled by a rate of holes going out from β-$FeSi_2$ as shown in Fig. 5. Even if the confinement of excitons can be realized, the excitons are dissociated by thermal activation and the some holes as a part of them goes out before radiative recombination at the β-NCs.

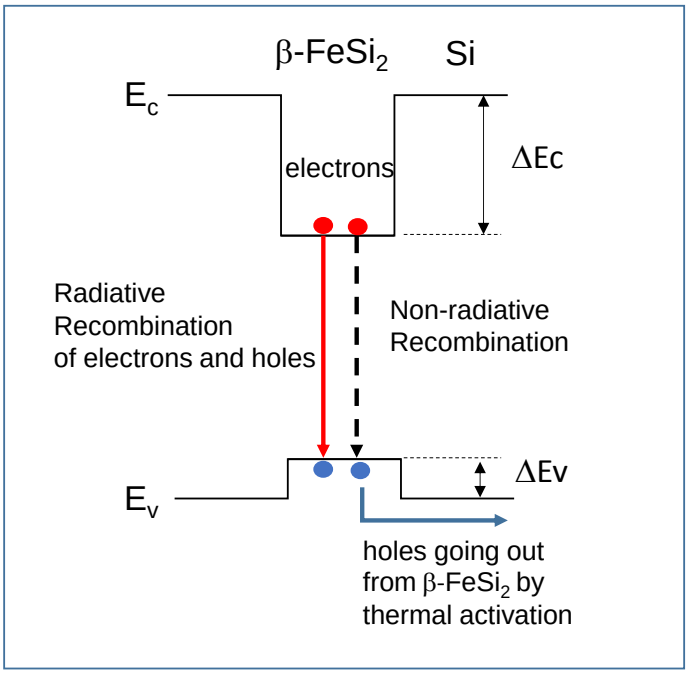
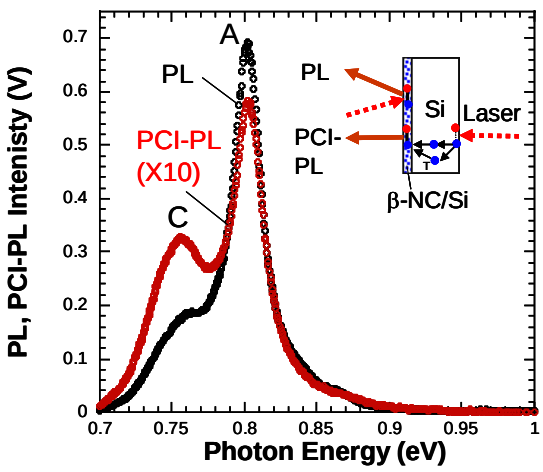


Figure 5

Band diagram in β-$FeSi_2$/Si heterointerfaces. ΔE_c and ΔE_v are band offset energies at the conduction and valence bands, respectively. Radiative recombination processes (RRP) between electrons at the conduction band and holes at the valence band and non-radiative processes due to escape of holes from β-$FeSi_2$ to Si. The RRP rate may be controlled by NRRP due to escape of holes.

Therefore, the RRP efficiency is controlled by the escape process of holes. Photocarrier-injection PL (PCI-PL) measurements is powerful in order to know dynamic processes (migration, recombination, repeated trap processes during migration) of minority carriers. The arrangement of PCI-Pl measurements is shown in Fig. 6. The big difference between PL and its measurements is the way of their excitation light (usually lasers with suitable power and wavelength). In the PCI-PL measurements, the Si substrate is irradiated by the laser and pairs of electrons and holes are optically generated near the back-side surface. The minority carrier can diffuse into the reverse side (toward β-$FeSi_2$) frequently is trapped at the trap centers due to doped impurities.

In cases of Cu-doping where we observed pronounced enhancement of the A band emission in Fig. 4, we think that such a dynamic migration process of minority carriers (holes) are related to the PL enhancement. Under this assumption, we investigated the PCI-PLs in Fig. 6, dependences of excitation frequency on their intensity and phase-shift in Fig.7 (response delay due to migration rate, or trap frequency).



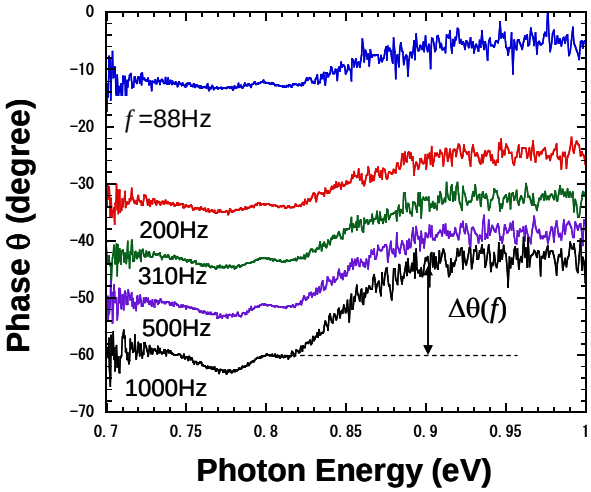


Figure 6 (left) PL and PCI-PL spectra for Cu-doped β-NC/Si nano-composite phases on substrates (see the in-set). The both spectra were measured at 8 K. This sample was annealed for 5.5 h. The PCI-PL spectrum includes information of holes migration with a repeated trap process and radiative recombination of electrons and holes at the β-NCs.

Figure 7 (right) Phase spectra of PCI-PL measured at each excitation frequency (chapping frequency of excitation laser). $\Delta\theta(f)$ is defined as a difference in phases at ~0.8 and ~0.9eV.

Figure 7 shows the phase spectra of PCI-PL signals measured at each frequency *f*. We observed clear phase-changes in the energy region where the A and C emissions in PL and PCI-PL spectra were observed. This result indicates that these phase-changes are attributed to migration of minority carriers (holes in this study) from back-side of n-Si substrates to the β-NCs. We also observed a pronounced frequency dependence of the phase spectra as the frequency increased. Phase shift (Δθ) is defined as a difference in phases at emission bands at ~0.8 eV and the non-emission region at ~0.9 eV and can be regarded as a delay response due to the migration of holes with a repeated trap process brought by Cu-doping into n-type Si substrates.

Therefore, we can deduce a time constant (τ) of such a delay response from frequency dependence of the Δθ by using the following equation;

$$\Delta\theta(f) = 360\tau(s)\cdot f(Hz) + \Delta\theta(0) \quad (in\ degrees),$$

where $\Delta\theta(0)$ is an off-set of phase shift coming from some mechanical reasons.

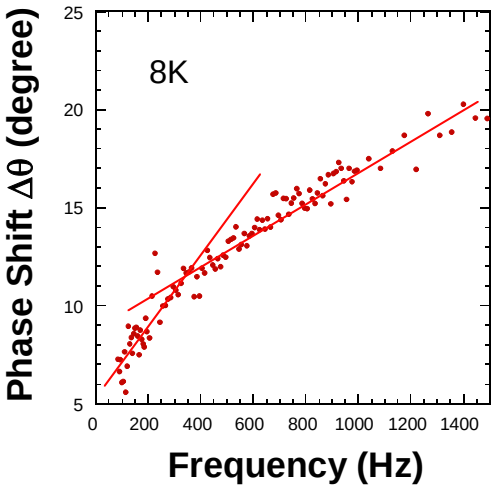


Figure 8

Phase shift (Δθ) defined in Fig. 7 as a function of frequency. Two slopes were observed and mean two delay responses with different time constants τ_1=87.8 μs and τ_2=21.8 μs for migration of holes. The longer time constant obtained by this analysis corresponds to migration process with repeated trap process of holes. This trap comes from Cu-doping. However, the measurements at 50 K the time constant was close to that in usual Si substrates. This fact suggests that the energy depth of trap may be 4~5 meV.

The $\Delta\theta$ was computed from the PCI-PL phase spectrum at 8 K as a function of the frequency *f*. We found two slopes with different time constants τ_1 and τ_2 in Fig.8 and obtained two time constants τ_1=87.8 μs and τ_2=21.8 μs. This τ_2=21.8 μs is the same to τ= 22 μs obtained in the non-doped β-NCs. These results are very important and indicate that doping of Cu atoms into n-Si substrates introduces a hole migration process with larger τ_1 which may be attributed to an repeated trap process of holes.

PCI-PL measurements reveal that enhancement of the A band emission is attributed to controlled migration of holes with the repeated trap process due to Cu-doping into the Si phase. However, this trap center may form a shallow energy well of 4~5 meV so that the migration control of holes above 50 K is not effective to enhancement of PL. For light emission possible at room temperature, we need formation of trap centers with energy well of more than 26 meV.

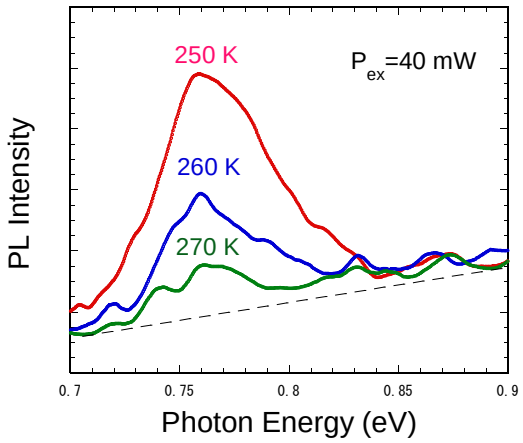


Figure 9

PL spectra from the oxidized non-composite phases near room temperature. The oxidation of β-NCs/Si nano-composite phase was carried out at 900°C for 6 hours. The FTIR absorption measurements revealed that the Si phase was mainly oxidized. This means that a β-NCs/SiO_2 nano-composite phase forms. SiO_2 has a wide band-gap and makes large offset energies for both conduction and valence bands with β-$FeSi_2$. So we can expect sufficient confinement of electron-hole pairs at the β-NCs in the oxidized nano-composite phase. This situation may contribute to observable PL spectra near room temperature.

5. Future study required moreover

Toward realization of room temperature light emission from β-$FeSi_2$ we need sufficient confinement of electrons and holes (or M-W excitons) in the β-NCs at room temperature. So we cannot expect it to β-NCs/Si hetero-structures because of the too small valence band offset as described above and shown in Fig. 5, and we need to change other hetero-structures fabricated in SiO_2 or SiC which can realize sufficient confinement of electrons and holes in the β-NCs and may give the maximum efficiency of radiative recombination except for non-radiative recombination processes due to the inherent interface problems. We have already observed enhancement of PL from β-NCs/SiO_2 hetero-structures which is fabricated by oxidation of β-NCs/Si hetero-structures and evident PL maintained near room temperature as shown in Fig. 9.

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