Extended Abstracts of the 2019 International Conference on Solid State Devices and Materials, Nagoya, 2019, pp889-890

Extended carrier lifetime in faceted PbS quantum dot superlattice fabricated by sedimentation method

R. Kimura[1], S. Sugisaki[1], T. Sugimoto[1], M. Fujishima[1], S. Watanabe[2], K. Mukai[1,2]

[1] Graduate School of Engineering Science, Yokohama National University.
[2] Graduate School of Engineering, Yokohama National University.
79-5 Tokiwadai, Hodogaya-ku,
Yokohama 240-8501, Japan
Phone: +81-45-339-3853 E-mail: mukai-kohki-cv@ynu.ac.jp

Abstract

We investigated the optical properties of a quantum dot (QD) superlattice film formed by the deposition of faceted colloidal PbS QDs in a solution. We observed that the emission lifetime at the excited states was extended by the formation of the superlattice. Promotion of QD alignment with the help of a Si template further extended the lifetime.

1. Introduction

Quantum dot (QD) superlattice solar cells have attracted attention in order to realize high photoelectric energy conversion efficiency. When QDs are periodically arranged three-dimensionally, the electron wavefunctions of the QDs overlap to form the intermediate bands, thereby suppressing heat loss and allowing light absorption of a wide range of wavelengths in the solar cell [1]. In order to fabricate QD superlattice, we have proposed the method to deposit structural symmetric colloidal QDs in solvent onto an array of inverted pyramidal holes (template) which was prepared by the anisotropic etching of a Si substrate. By depositing faceted PbS QDs, a superlattice film was successfully formed in which the facets face each other and the plane orientations of the constituent QDs are aligned [2]. In this study, we investigated the effects of deposition time and the presence of template on the optical properties of QD superlattice films.

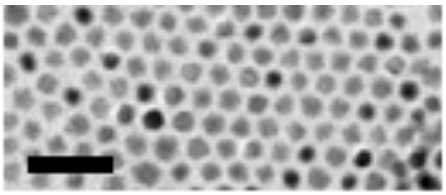
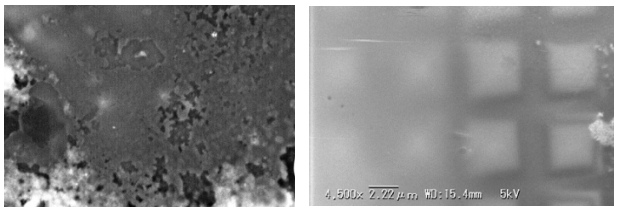


Fig. 1 TEM image of faceted PbS QDs. Scale bar is 20nm.

2. Experimental

By adjusting the synthesis conditions, the truncated octahedral QDs (Fig. 1) were synthesized [3]. Oleic acid was used as a ligand. By using anisotropic etching with the KOH solution, about 2-mm square template where inverse pyramidal holes having a side length of 3 μm were periodically arranged was prepared on a Si (100) substrate. PbS QDs were deposited on the template or a flat Si substrate to produce QD films. Before the deposition, Si substrate was immersed in a piranha solution for the hydrophilization treatment. This process reduces the affinity between QD and Si surface, and then promotes the free arrangement of QDs. During the deposition, the evaporation rate of the solvent was controlled by using a sealed container to adjust the preparation time of QD film in the range of 20 minutes to 7 days. The photoluminescence (PL) and emission lifetime of various QD films were evaluated.



(a) (b)

Fig. 2 (a) SEM images of QD film prepared under the conditions of (a) sedimentation time 20 minutes on a flat substrate, and (b) 7 days on a template.

3. Results and discussion

Figure 2 shows SEM images of the QD films prepared under the conditions of 20 minutes of sedimentation time on a flat substrate and 7 days of sedimentation time on a template. By prolonging the deposition time, a relatively flat and uniform film of surface texture was obtained.

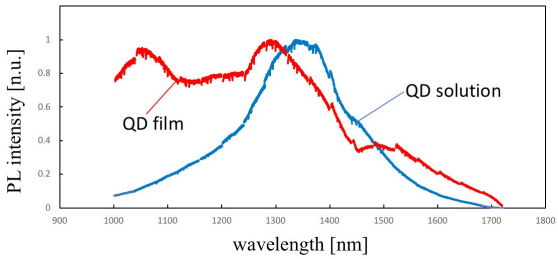
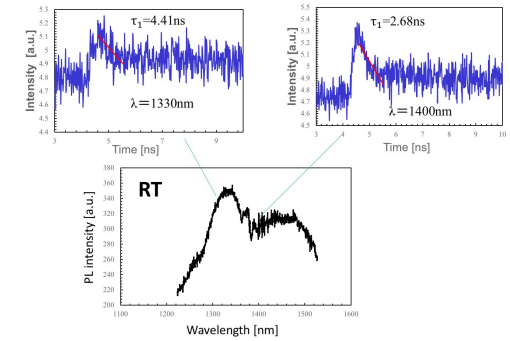
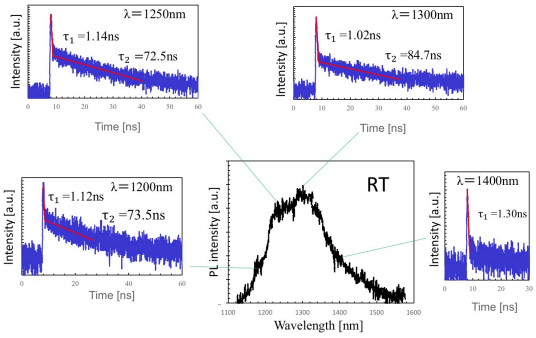


Fig. 3 PL spectra of QD film and QDs in the solution.

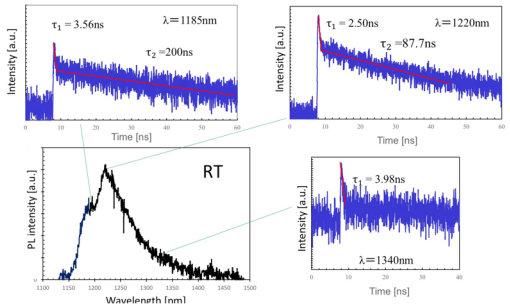
Figure 3 shows the PL spectrum of QD film prepared on a Si template for 7 days and that in a solution before deposition. By composing the film, the emission from the excited states became stronger. This result suggests the formation of intermediate bands at the excited states [4]. In the solution, the excited electrons relax immediately to the ground state and recombine with the holes, whereas when the intermediate bands are formed in the excited states, the excited electrons are de-localized and the recombination at the excitation states is promoted.



(a)



(b)



(c)

Fig. 4 PL spectra and decay curves: (a) QDs in a solution, and QD films (b) on a flat substrate and (c) on a template.

The emission lifetime was measured to verify the formation of the intermediate bands. Figure 4(a) shows the μ-PL spectrum of QD in a solution and the results of lifetime measurement. The emission lifetime of QD in solution was 5 ns or less regardless of the wavelength. The same evaluation result of the QD film on a flat substrate is shown in Fig. 4(b). The decay curves at long wavelengths, which corresponds to the ground state, were not much different from those of QD in a solution. But for the higher states, the double exponential decay curves had appeared. By the calculation of the two lifetime fittings, it was found that the short lifetime is several ns, which is almost the same as that of QD in a solution, while another lifetime is very long, about several tens of ns. The same evaluation results of the QD film on the template is shown in Fig. 4(c). The emission lifetime of the ground state was not much different from that of other two samples, and the double exponential decay curve appeared at the excitation state. It should be noted that the lifetime of 200 ns appeared at 1185 nm, which is quite longer than others.

Table I Emission lifetimes of QDs.

	λ (nm)	τ_1	τ_2
in solution	1330	4.41	-
	1400	2.68	-
on flat substrate, 20 min.	1200	1.12	73.5
	1250	1.14	72.5
	1300	1.02	84.7
	1400	1.30	-
on Si template, 7 days	1185	3.56	200
	1220	2.50	87.7
	1340	3.98	-

Table I is a summary of the lifetime measurements. τ_1 is the shorter lifetime and τ_2 is a longer one. All τ_1 values are on almost the same order, suggesting that they are the emission lifetime when no intermediate band is formed. On the other hand, long τ_2 is considered to be the carrier lifetime from the portion where the intermediate bands were formed. The prolongation of the emission lifetime occurs only at higher states. This would be because the long-chain oleic acid was used as the ligand for QD. The higher the state, the larger the spread of the wavefunction. The wide QD interval resulted in the wavefunction overlapping only at the sublevels of relatively high orders.

τ_2 at the higher order state in the template sample was more than twice that of the others. This is considered to be related to the spread area of the wavefunction in real space. The area of the region in which the intermediate band is formed is comparatively wider on the higher order states. The stronger the carrier delocalization, the longer the carrier lifetime. On a flat substrate, such increase in the lifetime of the higher-order levels was not observed. This would owe to the absence of the long-period alignment of QDs promoted by the template.

4. Conclusions

In the optical evaluation of the QD superlattice film formed by the sedimentation method, two emission lifetimes of several ns or less and several tens of ns or more were observed. It suggests that the regions where the intermediate bands were formed or not were mixed in the film. A longer emission lifetime was obtained in the film on a template, which would have resulted in the formation of wider intermediate bands.

Acknowledgements

This research was supported by the Nohmura Foundation for Membrane Structure's Technology.

References

[1] T. Nozawa, Y. Arakawa, Appl. Phys. Lett. **98**, 171108 (2011).
[2] K. Mukai, S. Fujimoto, and F. Suetsugu, Appl. Phys. Express **11**, 085601 (2018).
[3] M. A. Hines and G. D. Scholes, Adv. Mater. **15**, 1844 (2003).
[4] K. Mukai, Semicond. Sci. Technol. **30**, 044006, (2015).