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Formation of Perfect Superlattice with Aligned Plane Orientation of Colloidal PbS Quantum Dots

Satoshi Fujimoto, Fumimasa Suetsugu and Kohki Mukai

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

Abstract

We investigated the method to form a perfect quantum dot (QD) superlattice, in which each QD has the same plane orientation, by the deposition of colloidal PbS QDs with clear facets in solution. QD facets were controlled by synthesis temperature. We found that the slower the deposition, the better the orientation alignment of QDs. The energy conversion efficiency of solar cell is expected to be improved with perfect QD superlattice by its high carrier mobility in intermediate bands.

1. Introduction

Energy conversion efficiency of 70% or more is expected in the intermediate band type solar cell using quantum dots (QDs) [1]. For the purpose, it is necessary to realize QD superlattice in which uniform QDs are packed periodically and densely. Researches to prepare superlattice with epitaxially grown QDs are mainstream at present. Since it is difficult to prevent generation of crystal defects and shape deformation of QDs by the epitaxial method, breakthrough is required.

On the other hand, researches on colloidal QDs, which have uniform three-dimensional isotropic shape and can be produced in large quantities by chemical synthesis in flasks, are thriving in recent years. It is known that when colloidal QDs are deposited in a solution on a flat substrate, closest packing structure locally self-assembles in an area of several tens to several hundreds of nanometers. The resulting QD film is composed of a mixture of polycrystalline parts and amorphous parts. When the closely packed structure has a long periodicity of micrometer order or more (ideally, single crystal structure), it is expected to have a function as a superlattice film in the devices. We have reported the promotion of three-dimensional long-period arrangement of QDs by depositing QDs onto template [2].

In this work, we investigated the means to realize a prefect QD superlattice in which each QD has the same plane orientation. By fabricating QDs with clear facets, the physical and chemical interaction between assembled QDs were strengthened. When the individual QDs in the superlattice have the same plane orientation, the mobility of the carriers is improved, which would cause further improvement of energy conversion efficiency of QD superlattice solar cell [3].

2. Experimental

Colloidal PbS QDs were synthesized by controlling the size and facets by changing the synthesis temperature in the range of 110 to 180°C [4]. Shape of QDs was observed by transmission electron microscopy (TEM). The QDs were deposited in the toluene on a Si (100) substrate. The sedimentation time was controlled during formation of QD film by evaporation rate of the toluene.

Evaluation of the produced QD film was carried out by θ-2θ measurement and pole figure measurement of X-ray diffraction (XRD). In the θ-2θ measurement, the degree of preferential orientation of QD plane parallel to the substrate can be evaluated by determining the texture coefficient (*TC*) with the measured peak intensities [3]. *TC* is defined by

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{\frac{1}{n}\sum I(hkl)/I_0(hkl)}. \qquad (1)$$

Here, *I(hkl)* is the intensity of measured peaks, $I_0(hkl)$ is the database strength of the peaks, and *n* is the total number of peaks measured. When the QDs are arranged randomly, the *TC* of any peak takes a value of 1, and when the QDs are completely oriented in a specific direction, the peak takes the maximum value of *n*. In the pole figure measurement, the diffraction intensity is measured while sample is rotated in in-plane direction, Phi, with 2θ fixed to the peak angle. By repeating this process while changing the elevation angle, Psi, it can be evaluated whether the individual QDs in film are oriented in the same direction.

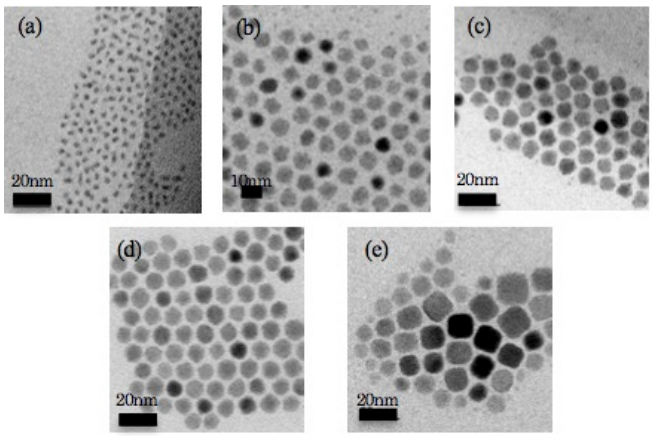

Fig. 1 TEM images of PbS QDs synthesized at (a) 110, (b) 150, (c) 160, (d) 170, and (e) 180°C.

3.Results and Discussion

TEM observation revealed that the shape of facets became more prominent as the size of QD increased. Figure 1 shows the results of QD-size and facet control depending on the synthesis temperature. QDs grown up to 170°C had a shape of truncated octahedron in which (111) plane and (100) plane were preferentially. However, at 180°C, the priority of (100) plane was high and QDs had simple cube shape.

QD films were fabricated by the sedimentation in the QD solutions. Figure 2 shows XRD spectra of QD films evaluated by θ-2θ measurement. Four peaks were observed, corresponding to the orientations of (111), (200), (220), and (311). Intensity ratio of each peak varied depending on the synthesis temperature and sedimentation time. Peaks of (111) and (220) dominated in the synthesis temperature range of 110 to 170°C. A (200) peak was preferentially oriented at 180 °C. Figure 3 shows *TC* of 170-°C and 180-°C sample. It was confirmed that the preferential orientation becomes stronger by increasing the sedimentation time from 20 minutes to 6 days.

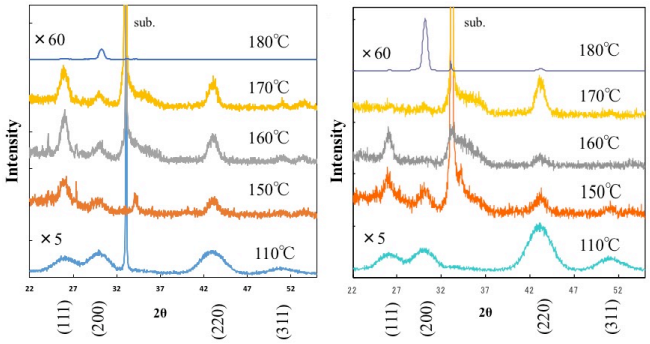

Fig. 2 XRD pattern of QD film deposited for (a) 20 minutes and (b) 6 days.

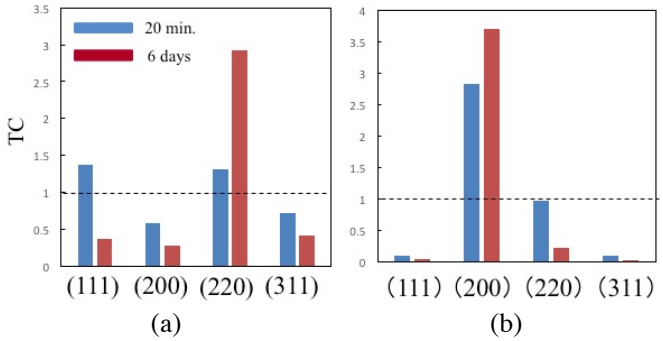

Fig. 3 Texture coefficient of QD films. Synthesis temperature of QDs was (a) 170°C and (b) 180°C.

In the pole figure measurement, a ring-like intensity distribution indicating that the sample was preferentially oriented in the same direction as confirmed by θ-2θ measurement. The ring-like distribution became clearer by slow sedimentation. Figure 4 indicates that the ring-like shape of 180-°C sample was very sharp, suggesting strong orientation. The distribution suggests that QDs of cubes as shown in Fig. 1(e) were stacked with touching (100) facets with rotating and sliding freely (Fig. 5 (b)). The pole figure map of 170-°C sample showed (220) orientation which was relatively loose. The result was consistent with *TC* measurement. We found that the plane orientation alignment of 170-°C sample was not good as compared with 180-°C sample. This might be because stacking of truncated octahedron structure of 170-°C sample is more complex than that of cubic structure of 180-°C sample (Fig. 5).

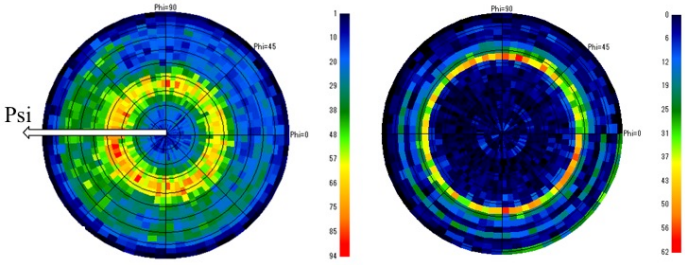

Fig. 4 Pole figure maps of QD films formed by sedimentation for 6 days. QDs were synthesized at (a) 170°C and (b) 180°C.

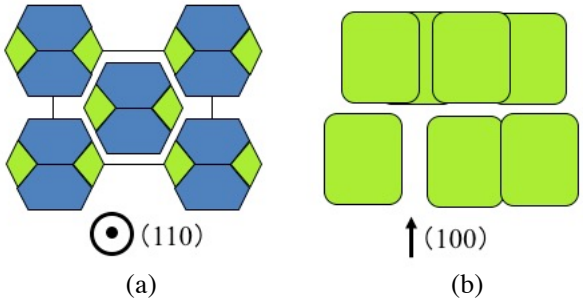

Fig. 5 Schematics of QDs stacked in film. Synthesis temperature of QDs was (a) 170°C and (b) 180°C.

4. Conclusions

We investigated the method to fabricate perfect superlattice in which the plane orientations of individual QDs are matched. We succeeded in controlling QD facets by synthesis temperature. We improved plane orientation alignment of QDs in superlattice film by controlling sedimentation time with the aid of facets.

Acknowledgements

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