Self-assembled colloidal PbS quantum dots on GaAs substrates

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Abstract. We report the fabrication and analysis of self-assembled monolayer and bilayer films of colloidal PbS quantum dots (QDs) on GaAs (001) substrates. 1,6-hexanedithiol is used as link molecule between QDs and GaAs substrates. Atomic force microscopy (AFM) and photoluminescence (PL) measurements confirm the formation of PbS QD film on GaAs. For the monolayer PbS QD film, the temperature-dependent PL shows a feature typical of close-packed film. For the bilayer PbS QD film fabricated from two different mean-sized PbS QDs, we find that the stacking sequence of QDs with different size affects the quantum yield and emission wavelength of the film.

1. Introduction
Colloidal quantum dots (QDs) are characterized by their high fluorescence efficiency, narrow spectral emission and broadly tunable color-emission. These properties, combined with the high photochemical stability, are expected to increase the device lifetime at the high luminescence and current regimes necessary for lighting applications.1 Among such QDs, PbS QDs are receiving great attention due to the narrow energy gap relevant for optical applications in the near-infrared region such as long wavelength telecommunications, photovoltaics, and bioimaging in low absorption of biological systems.2-4 In particular, the integration of colloidal semiconductor QDs on substrates to form two-dimensional arrays is becoming a promising field of scientific research due to their potential applications in microelectronics.5

In this work, we describe the assembly and photoluminescence (PL) characterization of monolayer and bilayer of PbS QDs on GaAs substrates. The PL intensities of monolayer PbS QDs show increase followed by rise in temperature, which is a feature typical for close-packed PbS QD films in agreement with our previous report.6 For the bilayer PbS QD films fabricated from two PbS QD ensembles with different mean sizes, we find that different stacking sequence of QDs with different size affects the quantum yield and emission wavelength of the bilayer film.

2. Experimental details
PbS QDs were synthesized using an organometallic route previously reported.7 The resulting PbS QDs were precipitated from the reaction mixture with methanol and redispersed in tetrachloroethylene (TCE). PbS QDs with two different mean sizes (3.6 and 4.1 nm dia.) were used in this work.

The GaAs wafers were cleaned in an ultrasonic bath with acetone and 2-propanol, and dried in a stream of nitrogen. Surface oxide was then removed by a 80 s etch in concentrated (35%) HCl followed by rinse with deionized water and 2-propanol. Surface modification of the GaAs wafers was
performed in a solution containing 90% 2-propanol and 10% 1,6-hexanediol (volume ratio) for 8 h in dark at room temperature. The surface modification was followed by several thorough rinses with 2-propanol. The self-assembly of monolayer PbS QDs was performed in a TCE solution containing PbS QDs for 12 h in dark at room temperature. After assembly the samples were thoroughly rinsed with TCE and dried with a stream of nitrogen. The bilayer samples was fabricated by repeating dipping in 1,6-hexanediol solution and PbS QD solution. Figure 1 shows the schematic description of the monolayer and bilayer films of PbS QDs on GaAs.

The 860 nm beam from a continuous-wave Ti:sapphire laser was used as an excitation source for the PL measurements. The samples were mounted in a compressed helium cryostat under vacuum to avoid air-exposure.

![Schematic diagram of PbS QDs on GaAs](image1)

**Figure 1.** Schematic description of monolayer PbS QDs of two different sizes on GaAs (samples A and B) and bilayer PbS QDs on GaAs with different stacking sequences (samples C and D). The black lines represent 1,6-hexanediol link molecules.

![AFM images](image2)

**Figure 2.** AFM images of (a) the untreated (001) GaAs substrate and (b) monolayer PbS QDs assembled on GaAs (Sample A).

### 3. Results and Discussions

To assess the coverage of the PbS QDs on the GaAs substrate, atomic force microscopy (AFM) was performed using SII Nanotechnology SPA300/E-SWEEP with Nanonis QC4-S. The topography of the samples was measured immediately after assembly, under vacuum with a base pressure below $10^{-5}$ Pa at room temperature. Figure 2 shows the AFM images of the untreated GaAs substrate and the PbS QDs (~3.6 nm dia.) assembled on GaAs substrate. The images shown are typical of images measured in several different areas of the substrate. The untreated GaAs shows a peak-to-valley roughness of less than 1.32 nm. The PbS assembled GaAs shows dot-like features with heights of up to 4.71 nm and typical lateral sizes of 10–15 nm. The lateral sizes of the AFM images are several times larger than the actual size of the QDs used (~3.6 nm), which is due to the AFM tip diameter (~20 nm). Considering the AFM tip diameter, this image is consistent with coverage of disordered QD monolayer on the GaAs surface.
Figure 3 shows PL spectra of samples A and B measured at 4.2 K. The emission of GaAs is observed at higher energy edge, which is not shown here. The emission peaks of samples A and B are located at 1100 and 1340 nm due to the different sizes. The emission peak is not Gaussian unlike the solution spectra, which is probably caused by energy transfer between QDs in the close-packed film. Figure 4 shows the integrated PL intensities of sample A as a function of measurement temperatures. Sample B shows the similar behaviour with that of sample A. The PL intensity shows increase followed by decrease with rise in temperature. According to our previous report, the increase followed by decrease in PL intensity with rise in temperature is a typical feature of close-packed PbS QD films and can be explained by thermally activated electronic transfer as shown in inset of Figure 4.

Figure 5 shows PL spectra of samples A, B, C and D measured at 4.2 K. We try our best to insure that the measurements are fulfilled under the same condition so that we can compare the four samples quantitatively. Compared with sample B, both samples C and D exhibit stronger emission due to energy transfer from smaller to larger QDs. Klimov et al. showed the evidence of rapid directed energy transfer in a bilayer structure comprising differently sized core-shell CdSe/ZnS QDs bound by dithiol linkers. Further, funnel-like band gap profiles are realized applying layer-by-layer assembly to CdTe nanocrystals of distinct sizes, which greatly improves the PL quantum yield of the QD films. However, to our best knowledge, there is no report on the effect of stacking sequence of the bilayer structures on PL behavior of films. Our results indicate that the stacking sequence of bilayer structure comprising different sized QDs affects the quantum yield and emission wavelength of the films thus prepared. Compared with emission peak of sample B, the PL peak of sample C exhibits blueshift and that of sample D exhibits redshift. However, the emission intensity of sample C is stronger than that of sample D. These abnormal phenomena are explained as followed.

For the surface modified GaAs wafers, many thiol molecules are distributed on the surface of GaAs, which serve as anchor to catch QDs in solution to form single monolayer close-packed QD film. To stack the second QD monolayer on top, the first QD monolayer has to be modified by another thiol molecule layer on the surface of the first QD monolayer. However, in this case, the quantity of available thiols serve as anchor to catch the next QD monolayer would be less than that on the GaAs wafer since it is unlikely that thiol molecules form a self-assembled layer as it did on the GaAs substrate. Also considering the probability that a thiol molecule catches a QD, there would be less QDs on the second monolayer than on the first monolayer. As a result, the mean distance between adjacent QDs is larger than that of the first monolayer.
According to the discussion above, the mean distance between larger QDs (the second monolayer) in sample C should be larger than that of sample B. The larger distance between QDs induces smaller energy transfer rate. As we discussed previously\(^6\), the energy transfer occurs in close-packed QD films due to inhomogeneous size distribution, which induce the redshift of emission line of QDs in close-packed film. Therefore, the blueshift of emission line of sample C compared with sample B is due to larger distance between the QDs in the second monolayer.

The smaller QDs serve as donors in bilayer films. Hence, there are more donors in sample C than in sample D according to our discussion. The energy transfer from smaller to larger QDs increases with the number of donors. Therefore, the stronger emission from sample C can be attributed to the existence of more donors.

![Figure 5. PL spectra of samples A, B, C and D measured at 4.2 K under the same conditions](image)

4. Conclusion

In summary, monolayer and bilayer structures of PbS QDs on GaAs have been fabricated. AFM and PL measurement confirm the formation of PbS QD film on GaAs. The monolayer structure exhibits typical PL feature of close-packed film. For the bilayer structure fabricated from two different mean-sized PbS QDs, the stacking sequence of smaller and larger QDs affects the quantum yield and emission wavelength of the films thus prepared.

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