

Thin film fabrication of CdS quantum dots on GaAs substrate by surfactant self-assembly

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In this study, cadmium sulfide (CdS) quantum dots (QDs) were synthesized using a microemulsion-based synthesis method, in which two microemulsions containing precursors of Cd^{2+} and S^{2-} , were mixed to form CdS QDs. The time-course variation in the average particle size was measured by UV-visible absorption spectroscopy. Subsequently, a thin film of CdS QDs was fabricated using a self-assembled monolayer (SAM) technique. First, undoped GaAs (100) wafers were cleaned and etched using HCl aqueous solution, and a SAM of 1,6-hexanedithiol was formed on the etched wafer surface using a typical SAM technique. Finally, CdS-dithiol-GaAs structures were fabricated by immersing the SAM-coated wafer in dispersion solutions of CdS QDs. In the serial steps of the fabrication of CdS QD thin films, the wafer surface was analyzed, and thin film formation was confirmed by contact angle measurement, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS).

Key words: Cadmium sulfide, Quantum dots, Microemulsion-based synthesis, Self-assembled monolayer, Thin film fabrication.

Introduction

Quantum dots (QDs) are semiconductor nanoparticles that have crystalline structures with unique optical and photoelectrochemical properties due to quantum confinement effects [1]. QDs have broad absorption and excitation spectra at wavelengths from the ultraviolet to the visible light range, narrow size-tunable emission spectra, negligible photobleaching, high photochemical stability and size-controlled luminescence properties [1-3]. These optical and photoelectrochemical properties establish them as potential alternatives to traditional fluorophores in biosensors [1,3] and as attractive materials for next-generation photovoltaic solar cells [4-6].

In general, there are two methods for synthesizing QDs. The first method is the controlled nucleation and growth of particles in a solution containing chemical precursors of metal and anion sources, which is the most common method for preparing colloidal QDs. The second method is particle formation via deposition from the vapor phase on proper substrates in molecular beam epitaxy or metallo-organic chemical vapor deposition [4]. Among various solution-based methods, microemulsion-based synthesis is a method of using microemulsions (thermodynamically stable dispersions of two immiscible liquids such as oil and water in the presence of a surfactant) as nanoreactors, which are reverse micelles containing precursors of metal and

anions. The reverse micelles collide among themselves and exchange reactants; thus, nucleation starts at the edge of the micelles. The nuclei grow when more reactants are fed via intermolecular exchange [7, 8]. This microemulsion-based synthesis approach is a powerful, facile, and inexpensive method for fabricating QDs because it usually produces QDs with well-controlled particle sizes and shapes without expensive or specialized instruments and complex procedures [7,8].

In order to take a full advantage of QDs for their biosensor or solar cell applications, the QDs are usually incorporated into some specific devices as well-organized structures. For example, some studies reported the fabrication of well-organized QD structures such as arrays [4,9,10]. Moreover, other studies have demonstrated the self-assembly of QDs such as the Langmuir-Blodgett films [11, 12] and/or self-assembled monolayer (SAM) films [13-16]. Although these studies provide fundamental knowledge about the fabrication of QD thin films on solid substrates, the practical applications of the dense films of QDs on a practically important semiconductor substrate such as GaAs have not been thoroughly investigated.

In this study, cadmium sulfide (CdS) QDs with a well-defined size were prepared using a microemulsion-based synthetic method, and their thin films were fabricated on a GaAs wafer substrate using a SAM technique. In the serial steps of the fabrication of CdS QD thin films, the wafer surface was analyzed by contact angle measurement, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS), and the analysis results were interpreted in terms of surface chemical composition and structure.

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Experimental Details

Preparation and characterization of CdS QDs

First, two water-in-oil (W/O) microemulsion solutions were prepared by mixing an aqueous solution of 0.1 M sodium bis(2-ethylhexyl) sulfosuccinate (AOT; Sigma-Aldrich) with isooctane (Sigma-Aldrich). A small amount of cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; Sigma-Aldrich) aqueous solution was added to one microemulsion solution, and the same amount of sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$; Sigma-Aldrich) aqueous solution was added to the other solution. Argon gas was then purged into the microemulsion solutions for 10 min to remove dissolved oxygen. The two microemulsion solutions were vigorously stirred at 1,000 rpm for 1 h and mixed with each other in the dark using a dropping funnel. The final concentrations of cadmium nitrate tetrahydrate and sodium sulfide nonahydrate were 4×10^{-4} M, and the final concentration of AOT was 0.1 M. The ratio of water concentration to AOT concentration ($[\text{H}_2\text{O}]/[\text{AOT}]$, in molar concentration) was adjusted to 5. The resulting transparent and slightly yellowish mixture solution was gently stirred at 200 rpm for a predetermined reaction time from 10 min to 10 h. After the reaction, the solution containing CdS QDs was analyzed using a UV-visible (UV-vis) absorption spectrophotometer (Shimadzu UV-1650). From the UV-visible spectra, the average particle size of CdS QDs was estimated according to the relationship between the particle size (D in nm) and the wavelength of the first excitonic absorption peak (λ in nm) [17,18].

Fabrication and characterization of the thin film of CdS QDs

For the fabrication of thin films of CdS QDs, GaAs (100) wafers (100 mm, n-type, Si doped, Freiburger Compound Materials) were used as substrates. Prior to film formation, the oxide layer of the wafer surface was removed by etching the wafer for a specific period of time with 18.5% HCl aqueous solution (Sigma-Aldrich). For the formation of a SAM, the etched GaAs wafer was immersed in an ethanol (ACS reagent; Sigma-Aldrich) solution of 0.5 M 1,6-hexanedithiol ($\geq 97\%$; Sigma-Aldrich) for 24 h and dried for 30 min in a nitrogen atmosphere in a glove box. The SAM-coated GaAs wafer was then immersed in the CdS QD dispersion for 72 h, and it was rinsed with ethanol several times and dried in a nitrogen atmosphere. The surface of the GaAs wafer coated with the CdS QD thin film was characterized by contact angle measurement (FTA 125 Contact Angle Analyzer), AFM (Nanoman II; Digital Instrument), and XPS (ESCA2000; Micro Tech Co.). For AFM topography measurements, the GaAs wafer surface coated with the CdS QD thin film was scanned with a silicon nitride probe (MLCT; Bruker) at a constant set point value of 2.5 eV. For XPS measurements, a Mg $K\alpha$ X-ray with an excitation

power of 170 W was used with a 45° take-off angle. Wide scans and narrow scans were performed with 50 eV pass energy/25 W electron beam power and 15 eV pass energy/100 W electron beam power, respectively.

Results and Discussion

Preparation and characterization of CdS QDs

Fig. 1 shows the UV-vis absorption spectra of CdS QDs fabricated in the microemulsion solutions as a function of reaction time. The first absorption peak position is known to be closely related to the particle size of CdS QDs [17,18]. Yu et al. demonstrated an empirical relationship between the particle size measured by TEM and the first absorption peak position in their UV-vis absorption spectra as follows [18]:

$$D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29 \quad (1)$$

where D (nm) is the size of a given QD nanocrystal sample, and λ (nm) is the wavelength of the first excitonic absorption peak of the corresponding sample.

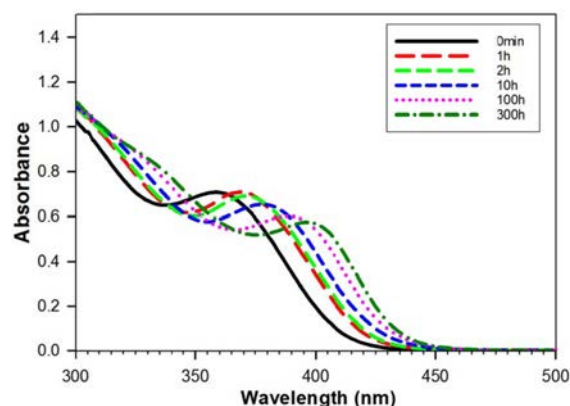


Fig. 1. UV-vis absorption spectra of CdS QDs obtained at different reaction times.

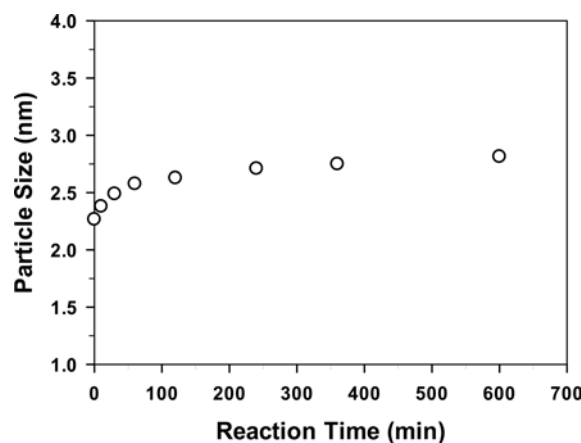


Fig. 2. Particle size of CdS QDs as a function of reaction time up to 10 h.

Nevertheless, this relationship holds only for the λ range of 260–470 nm. Based on the data in Fig. 1, λ ranged from around 360 nm to 400 nm; thus, the average particle size of QD particles was estimated to be approximately 2.3 to 3.4 nm for a reaction time of 300 h. As shown in Fig. 2, the particle size of the CdS QDs was steadily increased from 2.3 nm to 2.8 nm in 10 h, and it continued to increase to 3.4 nm until 300 h. In this study, the ratio of water concentration to AOT concentration (i.e., $W = [\text{H}_2\text{O}]/[\text{AOT}]$) was maintained at a constant value of 5 as variations can significantly affect the nucleation and growth of QD particles. According to the literature, a decrease in the W value typically decreases the particle size because water pools become smaller, which can usually cause a size reduction and thus a blue shift in both the absorption maximum and the absorption edge [19]. The blue shift of the absorption maximum and the absorption edge may be attributed to quantum confinement, and the smaller the particle size, the greater the blue shift.

Fabrication and characterization of the thin film of CdS QDs

In this study, the GaAs (100) wafers were cleaned with 18.5% HCl aqueous solution before SAM formation and thin film fabrication. According to a previous study [21], etching with HCl aqueous solution at an appropriate concentration removes more than 95% of gallium oxide and arsenic oxide, as well as carbon contamination.

As shown in Table 1, when the GaAs (100) surface was etched with the HCl aqueous solution, the contact angle was decreased from 57.5° to 36.8° whereas the root-mean-square (rms) surface roughness (estimated from the height profile of AFM topography) was increased from 0.26 nm to 0.59 nm. The current contact angle value of the GaAs surface before etching is consistent with the result of another study [22], and the reduced contact angle after etching may be attributed to the typical decrease in the acute contact angle for a heterogeneous surface with an increase in the rms surface roughness [23]. When the GaAs surface was

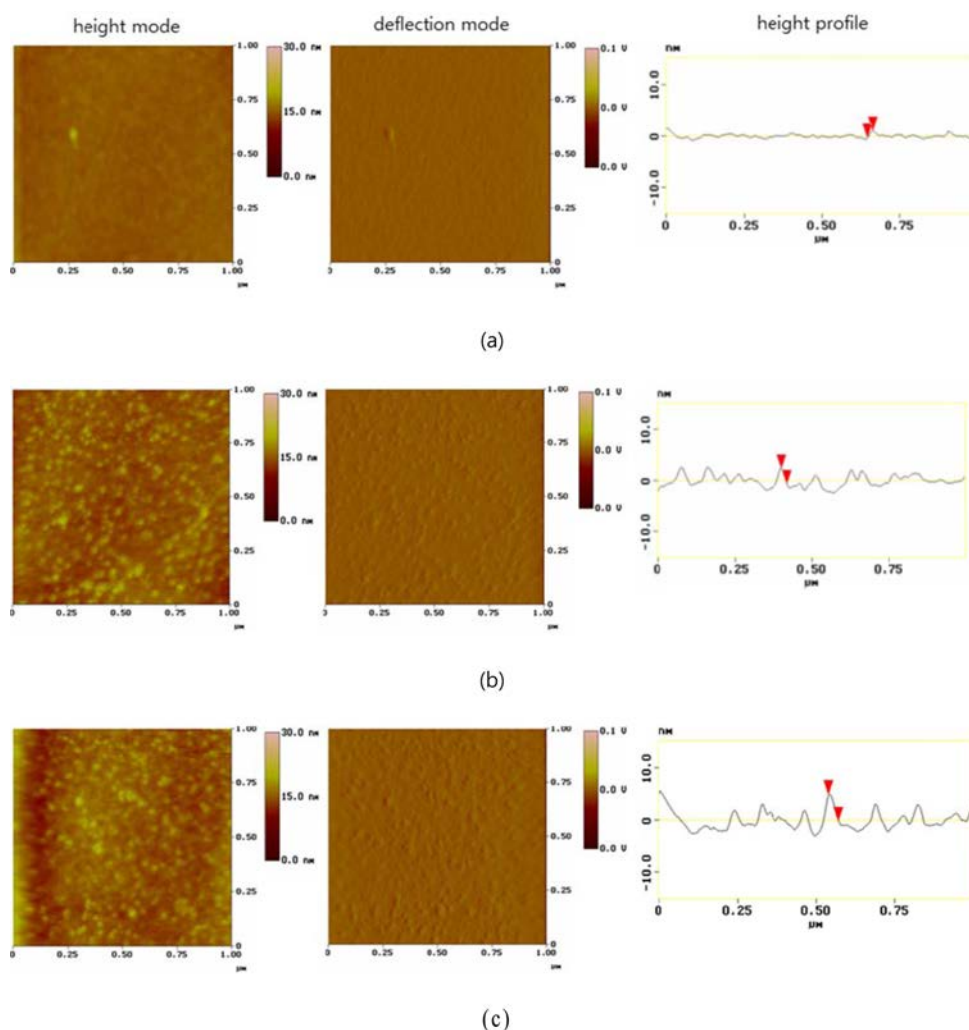


Fig. 3. AFM topography images and height profiles of GaAs (100) substrate after (a) etching with HCl aqueous solution, (b) deposition of the 1,6-hexanedithiol SAM, and (c) thin film fabrication of CdS QDs.

Table 1. AFM rms surface roughness and water contact angle of the GaAs (100) surface after washing with ethanol and deionized (DI) water, etching with HCl aqueous solution, deposition of the 1,6-hexanedithiol SAM, and thin film fabrication of CdS QDs.

GaAs (100) surface	AFM rms surface roughness (nm)	Contact angle (°)
Washing with ethanol and DI water	0.26	57.5 ($\pm$ 1.0)
Etching with HCl aqueous solution	0.59	36.8 ($\pm$ 0.9)
1,6-Hexanedithiol SAM	1.18	76.9 ($\pm$ 2.3)
CdS QD thin film	1.56	46.6 ($\pm$ 1.1)

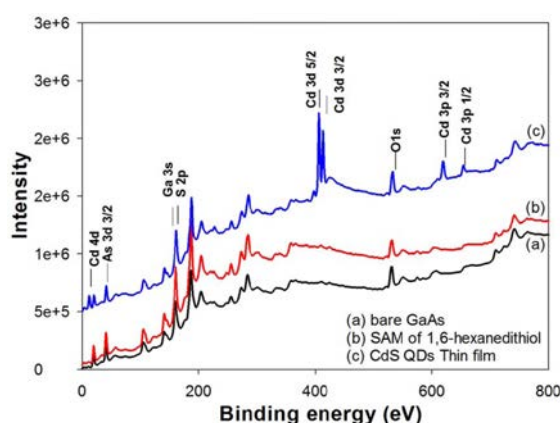
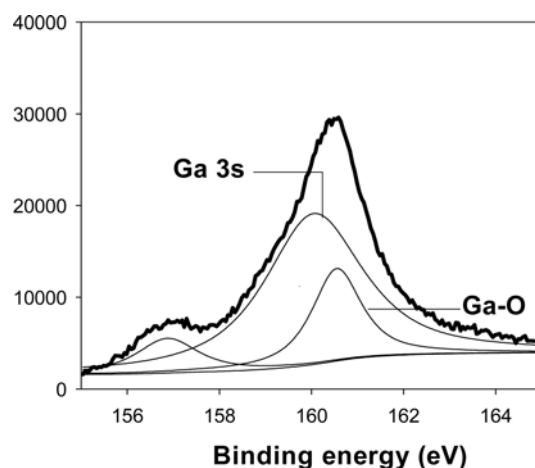


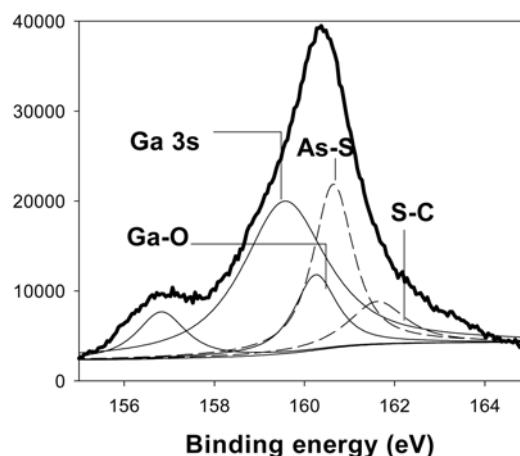
Fig. 4. Wide-scan XPS spectra of GaAs (100) surface after (a) etching with HCl aqueous solution, (b) deposition of the 1,6-hexanedithiol SAM, and (c) thin film fabrication of CdS QDs.

consecutively coated with the 1,6-hexanedithiol SAM and CdS QD thin film, the surface roughness was increased to 1.18 and 1.56 nm, respectively. The AFM topography images shown in Fig. 3 demonstrated the increase in surface roughness, and the thin film of CdS QDs had a disordered structure. A surface roughness of 1.18 nm for the 1,6-hexanedithiol SAM appeared to be reasonable considering that the thickness of a 1,8-octanedithiol ($\text{HS}-(\text{CH}_2)_8\text{-SH}$) SAM on Au surface was measured to be around 1.3 nm by XPS analysis [24]. On the other hand, when the GaAs surface was coated stepwise with the 1,6-hexanedithiol SAM and CdS QD thin film, the contact angle was first increased to 76.9° and then decreased to 46.6°. These contact angle values for the 1,6-hexanedithiol SAM and CdS QD thin film are consistent with the values (68° and 42.6°) for a 1,5-pentanedithiol ($\text{HS}-(\text{CH}_2)_5\text{-SH}$) SAM on Au and CdS QDs on Au reported in previous studies [25, 26].

Fig. 4 shows the wide-scan XPS spectra of the GaAs (100) surface after HCl etching, 1,6-hexanedithiol SAM deposition, and CdS QD thin film fabrication. Overall, there was no distinct difference between the wide-scan XPS spectra before and after deposition of the 1,6-hexanedithiol SAM. On the other hand, the XPS spectrum of the CdS QD thin film was noticeably



(a)



(b)

Fig. 5. Narrow-scan XPS spectra of the Ga 3s and S 2p levels of GaAs (100) surface after (a) etching with HCl aqueous solution, and (b) deposition of the 1,6-hexanedithiol SAM.

different from the two spectra of bare GaAs and the 1,6-hexanedithiol SAM in that it had some representative peaks of Cd; for example, Cd 3d_{3/2} and Cd 3d_{5/2} at around 405.7 and 412.5 eV. Fig. 5 shows the narrow-scan XPS spectra in the energy region of Ga 3S and S 2P as well as the deconvolution results (slim solid line). The deconvolution peaks clearly indicated that the spectrum for the 1,6-hexanedithiol SAM had peaks not only for Ga 3S and Ga-O but also for As-S and S-C bonding at around 160.5 and 161.5 eV, whereas that for the bare GaAs surface did not have the peaks of As-S and S-C bonding. The molecules of 1,6-hexanedithiol are known to form a stable, highly organized self-assembly of tilted, ordered alkyl chains, which can chemically bond to the bare GaAs surface as well as the CdS surface [27, 28]. Accordingly, the CdS QDs were bound to GaAs substrates, forming stable, disordered thin films mediated by the 1,6-hexanedithiol SAM; the result is consistent with the formation of CdSe monolayers on doped GaAs substrates [15].

Overall, the study demonstrated the successful fabrication of CdS QD thin films on a GaAs wafer surface via a 1,6-hexanedithiol SAM.

Conclusions

In this study, CdS QDs of a few nanometers in size were prepared using a microemulsion method, and their thin films were successfully fabricated on GaAs substrate by employing a SAM technique. Thin film formation was confirmed by contact angle, AFM surface roughness, and XPS measurements. These QD films have great potential to be applied to sophisticated biosensors and highly efficient photovoltaic cells by taking full advantage of their unique optical and photoelectrochemical properties.

Acknowledgements

This study was supported by the Dongguk University Research Fund (S-2017-A0434-00115).

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