Highly ordered CdS nanoparticle arrays on silicon substrates and photoluminescence properties

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Highly ordered cadmium sulphide (CdS) nanoparticle (NP) arrays were fabricated on silicon (Si) substrates using ultrathin alumina membranes as evaporation masks. The CdS NPs are polycrystalline and are composed of ultrasmall closely packed nanocrystallites. These crystallites increase in size as the duration of the CdS evaporation process increases. When the thickness of the NPs changes from about 10 to 50 nm, the size of the crystallites increases from about 5–14 to 20–40 nm. Photoluminescence measurements on the CdS NP arrays show a strong emission spectrum with two subbands that are attributed to band-edge and surface-defect emissions. The peak position and width of the band-edge emission band are closely related to the size of the crystallites in the CdS NPs. © 2005 American Institute of Physics. [DOI: 10.1063/1.1869545]

Nanometer-sized semiconductor particles, the so-called nanoparticles (NPs), have attracted much interest for the last two decades as they possess unique physical and optical properties that are closely related to their size.\textsuperscript{1–13} Semiconductor NPs are expected to exhibit quantum confinement effects when their size becomes comparable to the Bohr exciton radius, which results in an increase in the energy gap relative to that of the bulk solid.\textsuperscript{14} Among a variety of nanosized semiconductors, cadmium sulphide (CdS) has been intensively studied\textsuperscript{3–13} due to advantages such as a band-gap energy in the visible region ($E_g=2.5$ eV) and a relatively simple fabrication process. CdS NPs often present novel properties and have been widely used in solar cells, optoelectronics, and microelectronics. For the device application of CdS NPs, such as in electronic and optical areas, it is usually desirable to fabricate a large area array of CdS NPs. In many cases, high regularity of the CdS NP arrays is required to obtain precise control on the resultant device properties. Recently, structurally ordered CdS NPs have been fabricated in the pores of mesoporous materials.\textsuperscript{5,6}

As a well-established nanotemplate, porous alumina membranes have been widely used in the fabrication of many kinds of ordered nanostructures,\textsuperscript{14–20} especially after a great improvement in their pore regularity achieved using a two-step anodization process as proposed by Masuda.\textsuperscript{15} The porous alumina membrane can be attached to a suitable substrate to act as a nanotemplate for fabricating ordered nanostructures. Using ultrathin alumina membranes (UTAMs) as etching masks, nanohole arrays have been produced on various semiconductor materials, including GaAs,\textsuperscript{21} InP,\textsuperscript{22} Si,\textsuperscript{23} and ZnTe.\textsuperscript{24} Recently, using UTAMs as evaporation masks, we demonstrated the fabrication of ordered carbon nanotube arrays, initiated from ordered metal catalyst arrays, on Si substrates.\textsuperscript{25} In this letter, we report the realization of highly ordered large-scale CdS NP arrays on Si substrates using UTAMs as evaporation masks. The detailed structure and the photoluminescence (PL) properties of these arrays CdS NPs are also discussed. It will be shown that by changing the evaporation duration (the thickness of the deposited NPs), and hence varying the size of the crystallites in the NPs, it is possible to change the PL properties of the CdS NPs, including the peak position and width of the PL bands. The fabrication details of UTAMs on Si substrates can be found in our previous publication.\textsuperscript{25} After mounting of the UTAM on the substrate, thermal evaporation of CdS was carried out using an evaporation rate of approximately 0.2–0.3 nm/s. After completion of the evaporation, the UTAM was removed from the substrate using acetone, leaving the highly ordered CdS NP array on the surface of the substrate. Figure 1 shows the scanning electron microscope image of a typical NP array on a Si wafer, where part of the UTAM is left behind intentionally. The regularity of the pore arrays of the UTAM and the consequent CdS NPs is very high. The typical area of the UTAM is about 1.5 cm $\times$ 1.5 cm with our current setup and can be as large as 20–40 cm$^2$ with modified setup. The diameter of the deposited NPs has a monodisperse size distribution and can be adjusted from about 10 to 200 nm. In addition, there is a sieve-like CdS film formed on top of the UTAM.

A set of two samples (samples A and B) were characterized using x-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), and PL measurements. The two samples were fabricated with identical UTAMs and...
almost similar CdS evaporation conditions, except for the duration of the evaporation process which changes the thickness of the deposited films, i.e., the thickness of the NPs. The film thickness of samples A and B are about 10 and 50 nm, respectively. The substrates for these samples are n-type (001) Si covered with a 3-nm-thick silicon dioxide (SiO\textsubscript{2}) layer.

Figure 2 shows the microstructure of the CdS NPs of sample A. Figure 2(c) is the cross-sectional TEM image of four arrayed CdS NPs on the SiO\textsubscript{2}/Si substrate before removal of the UTAM. It can be seen that the NPs are located at the bottom of the apertures of the UTAMs and on the surface of the substrate. The thickness of the NPs is about 10 nm. Most NPs are flat disc-like particles. XRD measurement [Fig. 2(d)] indicates that the evaporated NPs are hexagonal CdS [indexed as Wurtzite CdS, S. G.: P\textit{6}\textsubscript{3}mc (186)]. Moreover, the CdS NPs exhibit a (002) preferred orientation, as revealed by the intensity ratio distribution among the diffraction peaks. It has been reported that thermally evaporated CdS films show a (002) preferred orientation as a natural result of the CdS thermal evaporation process.\textsuperscript{7,8} The width of the XRD peaks, especially the strongest peak of (002) at 26.5°, suggests a relatively small size of the CdS crystallites. The crystallite size of about 10 nm can be estimated from the width of the (002) peak by the Sherrer’s formula.\textsuperscript{26} This size is much smaller than the planar-size of the CdS NPs of about 50 nm, which possibly suggests that each CdS NP is a polycrystalline particle.

Cross-sectional HRTEM measurement [Fig. 2(a)] of a CdS NP of sample A indicates the polycrystalline nature of the NPs. We carried out the crystal-size estimation of the NPs in Fig. 2(a) by drawing the approximate crystallite boundaries in Fig. 2(b). Eight crystallites appeared in the cross-section plane of the NP. Thus, a single NP is estimated to be composed of about 30–40 closely packed small crystallites.\textsuperscript{27} The mean sizes of these crystallites are in the range of 5–14 nm,\textsuperscript{28} which is in good agreement with the estimated size of about 10 nm from the XRD measurement.

Figure 3 shows the microstructure of the CdS NPs of sample B. It was found that, as the thickness of the CdS NPs increases from about 10 to 50 nm, the shape of the NPs changes from flat discs to hemispheres. One of the hemispherical NPs is shown in Fig. 3(c), which is an enlarged image of a squared area in Fig. 3(a). The mean sizes of the crystallites of the NPs in sample B are in the range of 20–40 nm,\textsuperscript{28} which are apparently larger than that in sample A. This suggests that, as the evaporation progresses and the thickness of the NPs increases, the crystallite size also increases.

Room temperature PL spectra of samples A and B are shown in Fig. 4. We carried out a multipeak Gaussian fit to the PL spectra and found that both spectra consisted of two Gaussian fitted peaks (denoted as subbands I and II). Subbands I and II of sample A are centered at about 473 and 575 nm, respectively [Fig. 4(a)], while those of sample B are centered at about 506 and 563 nm, respectively [Fig. 4(b)].

According to previous studies,\textsuperscript{3–13} generally there are two PL emissions of CdS NPs, namely band-edge and surface-defect emissions. Band-edge emission is ascribed to the radiative recombination of excitons in the NPs. The PL peak energy of such band-edge emission is usually slightly lower than the band-gap energy of the CdS NPs. It is known that the band-gap energy of the NPs is related to the quantum confinement effect of excitons in the NPs. In the “quantum confinement region,” which is defined as the region with particle (crystallite) size smaller than 4 times the Bohr exci-
In summary, we have fabricated large-scale ordered CdS nanoparticle arrays on Si substrates using UTAMs as evaporation masks. The fabricated CdS NPs are polycrystalline and composed of small crystallites. The size of the crystallites in the CdS NPs increases as the duration of the evaporation process increases, resulting in the red-shift of the peak position of the band-edge PL emission of the CdS NPs. It is worth noting that, by adjusting the evaporation duration (thickness of the NPs), and hence varying the size of the crystallites in the NPs, it is possible to tune the PL properties of the CdS NPs, including the peak position and width of the PL bands.

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27In the simplified case of a round flat-disc with eight crystallites at the diameter line, there are about 30–40 crystallites in the discs.
28The mean size of a crystallite here is defined as the diameter of a sphere with the same volume of the crystallite.