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CdS/CdSe lateral heterostructure nanobelts by a two-step physical vapor transport method

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Abstract
The two-dimensional heterostructure nanobelts with a central CdSe region and lateral CdS structures are synthesized by a two-step physical vapor transport method. The large growth rate difference between lateral CdS structures on both ±(0001) sides of the CdSe region is found. The growth anisotropy is discussed in terms of the polar nature of the side ±(0001) surfaces of CdSe. High-resolution transmission electron microscopy reveals the CdSe central region covered with non-uniform CdS layer/islands. From micro-photoluminescence measurements, a systematic blueshift of emission energy from the central CdSe region in accordance with the increase of lateral CdS growth temperature is observed. This result indicates that the intermixing rate in the CdSe region with CdS increases with the increase of lateral CdS growth temperature. In conventional CdSSe ternary nanobelts, morphology and emission wavelength were correlated parameters. However, the morphology and emission wavelength are independently controllable in the CdS/CdSe lateral heterostructure nanobelts. This structure is attractive for applications in visible optoelectronic devices.

1. Introduction
Recently, II–VI nanostructures catalyzed by Au or other metals have attracted a great deal of attention since these structures offer unique properties useful for novel optoelectronic devices [1]. Among the various II–VI nanostructures, CdS and CdSe nanostructures are specifically promising for nanophotonic devices operating in the visible spectral range [2]. CdS and CdSe nanostructures have been extensively investigated to exploit the unique properties of these structures. Nanolasers [3], field effect transistors [4], photoconductive sensors [5] and other optoelectronic devices using these nanostructures have already been reported. Due to the inherent polar nature of the ±(0001) planes of the wurtzite (WZ) crystal structure, morphological evolution depending on the growth conditions has been reported [6]. Relative dominance between vapor–liquid–solid (VLS) and vapor–solid (VS) growth mechanisms determines the final shape of the nanostructures [7, 8]. Ternary CdSxSe1−x nanobelts (NBs) are particularly attractive because their optical emission energy can be continuously tuned from 1.72 to 2.42 eV by varying the S mole fraction, x (=[S]/([S] + [Se])). Therefore, emission energies from these ternary nanostructures cover the entire visible spectral range and thereby these nanostructures are particularly important for light-emitting devices. The growth and color tunable photoluminescence (PL) from ternary CdSxSe1−x NBs and nanowires (NWs) have been reported [9, 10] and even stimulated emission from CdSxSe1−x...
NBs by optical excitation has been observed [11, 12]. However, the incorporation rate of S species into NBs is strongly influenced by the growth temperature when these species compete with the Se species. In our previous report, we pointed out the difficulty in controlling S incorporation when these species compete with the Se species. In our previous report, we investigated the properties of CdS/CdSe lateral heterostructure NBs which could overcome this difficulty. Although ordered nanostructures grown by a multiple seeding technique have been demonstrated on CdSe NBs which serve as substrates [14], lateral heterostructure NBs have yet to be investigated.

2. Experimental details

CdS/CdSe lateral heterostructure NBs were grown by a two-step physical vapor transport method employing a conventional single zone furnace with 1 inch diameter quartz tube (Lindberg Blue M Mini-Mite). A quartz boat containing CdSe powder (200 mg, Alpha Aesar 99.999%) was placed in the center zone. Si substrates with surface dimensions of 1.2 cm × 2 cm were placed downstream from the center. Temperatures were calibrated with a thermocouple. Substrate temperatures were ~300°C lower than source temperatures. For convenience, the growth temperatures reported in this study refer to the source temperatures. Most of the CdS/CdSe nanostructures reported so far by other research groups were grown on 5–10 nm gold-coated Si substrates. However, in the present study, we employed a commercially available 10 nm ± 1 nm gold colloidal solution (Ted Pella) with a particle density of 5.7 × 10¹² ml⁻¹. First, oxide-free, hydrogen-terminated Si substrates prepared by diluted HF dipping were dipped in commercial poly-L-lysine solution for 1 min. Then, the gold colloidal solution was dispersed on the substrate and rinsed with deionized water after 1 min. The existence of evenly distributed gold particles was confirmed by scanning electron microscope measurement. H₂(10%)/N₂ forming gas with a flow rate of 200 sccm min⁻¹ was introduced as the carrier gas. CdSe NBs were grown under optimized growth conditions (2 h at 900°C). The sample was then cooled down to room temperature while maintaining the flow of the forming gas. The quartz boat was quickly changed with another quartz boat containing CdS powder (200 mg, Alpha Aesar 99.999%) to grow CdS lateral structures for 2 h at 700, 750, 800 or 850°C.

The morphologies of as-grown samples were observed by scanning electron microscopy (SEM, JEOL JSM-6700F). Transmission electron microscopy (TEM) specimens were prepared in the following manner. The NBs with the substrate were immersed in a container with ethanol and the container sonicated for 20 s in order to remove the NBs from their underlying substrates. These NBs were then dispersed onto a holey carbon film. TEM investigations were carried out in a Philips Tecnai F20 equipped with an energy dispersive x-ray spectroscopy (EDS). Micro-photoluminescence (μ-PL) measurements of single CdS/CdSe lateral heterostructure NBs were carried out employing a home-built μ-PL system. A 325 nm He–Cd laser with random polarization (Melles Griot 40 mW) was guided into a modified commercial microscope (Olympus BX60M) with a commercial filter cube (U-MWV2) consisting of an excitation filter, a barrier filter and a dichromatic mirror. The laser beam was focused to a spot size of 2 μm by an objective lens (Olympus 100×, NA = 0.9). μ-PL from a single nanostructure was collected by the same objective lens. The filter cube blocked the 325 nm laser line and allows wavelengths larger than 430 nm. By using a commercial dual-port attachment, imaging by a charge-coupled device (CCD, imaging source DBK41AF02) and spectroscopic measurements were done simultaneously. For spectroscopic measurements, the μ-PL signal was introduced into a multimode fiber using a fiber-launching module dispersed by a 0.5 m monochromator (Dongwoo Optron) and detected by a photomultiplier tube (Hamamatsu R928). For single nanostructure measurements, NBs were transferred to an Si substrate after brief sonication in toluene. The density of the dispersed NBs enabled us to obtain a PL signal from an isolated NB. All measurements were done at room temperature.

3. Results and discussion

Figure 1(a) shows a SEM image of heterostructure NBs for CdS lateral structures grown at 800°C. Tapered NBs with high production yield are observed. From the previous investigation [13], CdSe NBs with WZ structure grew along the [0110] direction with ±(0001) side and ±(2110) top/bottom surfaces. Together with prevailing NBs, NWs with a much lower production yield are also observable. These NWs may have different origins due to local temperature fluctuations and/or gas flow dynamics variations. In the present study, we only focus on the NBs.
Based on extensive plan-view SEM investigations, all samples grown at 900 °C for the CdSe central region but with different CdS growth temperatures from 700 to 850 °C look similar. The heterointerface between CdS and CdSe is not clearly discernible from the SEM images. Thus we transferred NBs to the Si substrate and the NB images are detected by a backscattered electron detector. As shown in figure 1(b), the heterointerface can now be clearly observed by SEM. CdS grew laterally on both the ±(0001) surfaces of the central CdSe. Figures 1(c)–(f) show the SEM images of a series of NBs grown at different CdS formation temperatures. From these figures, a few important observations could be made regarding the CdS lateral structures. The lateral growth rates of CdS from both sides of the CdSe are quite different. This growth rate anisotropy becomes more significant on increasing the CdS growth temperature. Self-catalyzed growth could take place predominantly on the chemically active, positively charged Cd(cation)-terminated (0001) polar surface of the NB provided there is sufficient thermal energy to surmount the nucleation barrier. However, the growth rate on the chemically inert, negatively charged Se/S(anion)-terminated (0001) side surface of the NB is relatively low. This growth mechanism has been suggested in terms of a spontaneous polarization-induced asymmetry growth mechanism by Ma et al [15]. Therefore, the wider lateral regions are formed on the Cd-terminated surface of pre-existing CdSe NBs. When the growth is dominated by the VLS mechanism, the nanostructures tend to form NWs. This type of growth occurs at low substrate temperature when the vapor supply is low. Increasing the source temperature in a conventional single zone furnace increases both the vapor supply rate and the substrate temperature. This results in the VS growth mode becoming more dominant and to compete with the VLS mechanism [8]. It is interesting to note that there is a tapering effect on the central CdSe NBs. Growth predominantly occurs at the Au–semiconductor interface along the direction via the VLS mechanism. Nevertheless, the VS growth mechanism is also present, which results in tapering of the central CdSe region as the bottom part of the NB has been subjected to longer growth time than the top (tip) part of the NB. However, the situation is quite different for the CdS lateral growth. During the growth of CdS lateral structures on the CdSe NBs, the entire CdS/CdSe lateral heterostructure NB from the tip to the bottom is subjected to the equivalent growth time. Therefore, the width of the CdS lateral structure should be uniform along the lateral direction if the nucleation barrier is only responsible for lateral growth. However, it is obvious that the CdS lateral structure from a cation-terminated surface is much wider at the bottom part of the NBs, especially for samples grown at high temperatures (figures 1(e) and (f)). This interesting result could be explained in terms of the surface diffusion of species. Due to the low nucleation rate on the top/bottom ±(2110) surface, CdS species arriving at these surfaces will diffuse and incorporate onto the ±(0001) side surfaces which offer numerous nucleation sites. Since the bottom part of the CdSe NB provides a larger collecting area for the CdS species, the total number of species for incorporation into side surfaces increases dramatically compared to the narrow part near the tip which offers only limited collecting area. This effect results in the CdS lateral growth rate difference along the length of the NB. This phenomenon is similar to that commonly used in selective-area growth where the masked/patterned substrate is used to locally enhance the growth rate in the opening/window regions [16]. In addition, it is noteworthy that no axial growth is observed during CdS lateral structure growth. According to VLS theory, species supplied from vapor are diffused into the liquid-state catalyst. When species are supersaturated, the preferential nucleation which leads to axial growth occurs at the liquid/solid interface. During the growth of material A on material B for NW heterostructures, the sign of the interfacial energy difference, \( \Delta \sigma = \sigma_{\text{Au}} - \sigma_{\text{A}} + \sigma_{\text{B}} - \sigma_{\text{Au}} - \sigma_{\text{B}} \) determines the morphology of nanowire heterostructures where \( \sigma \) is the interfacial energy. If the difference is positive, island growth at the liquid/solid interface is favorable and leads to kinked nanowire growth [17, 18]. The interfacial energy between Au and CdS is presumably larger than that between Au and CdSe. Unlike nanowire heterostructures, our CdS/CdSe lateral heterostructure NBs may choose the other growth route (i.e. the termination of axial growth) rather than kinked growth to reduce the total Gibbs free energy.

Figure 2(a) shows a low magnification TEM image of a typical CdS/CdSe lateral heterostructure NB where the central CdSe and lateral CdS regions are clearly visible. Figure 2(b) shows a high-resolution TEM image near the CdS/CdSe heterointerface. The heterointerface is well defined and the lateral CdS region is defect-free. Selected-area electron diffraction (SAED) investigation taken from the CdS lateral region shows a well-defined single set of diffraction spots (not shown here), further confirming the single-crystalline nature of CdS. However, the TEM image at the central CdSe region shows a defective structure, indicating that this region is probably covered with non-uniform, ultra-thin layer/islands.
To clarify this, SAED was taken from this region and an example is shown in figure 2(c), in which two sets of electron diffraction patterns overlapped with each other can be seen with both being WZ crystals. This is in agreement with our high-resolution TEM studies. A barely traceable amount of Se element, presumably due to the probing beam size effect, is detected by EDS analysis from the lateral CdS, suggesting that lateral structures are pure CdS. In contrast, however, a substantial amount of S element is detected in the central CdSe region as shown in figure 2(d). The elemental analysis reveals that the S mole fraction, \(x = \frac{[\text{Si}]}{([\text{Si}]+[\text{Se}])}\) is about 0.3.

Figure 3(a) shows the \(\mu\)-PL spectra from CdS/CdSe lateral heterostructure NBs with different CdS growth temperatures together with those from CdS and CdSe NBs for reference. Two near-band-edge PL peaks are observed for all heterostructure samples. The peaks at 510 nm coincide with the peak from the reference CdS NBs and originate from the CdS lateral structure. Their spectral positions and linewidths are insensitive to the growth temperatures of the CdS lateral structures. However, the PL peaks at longer wavelengths are related to the emission from the central regions. This is confirmed by color \(\mu\)-PL imaging results as shown in the inset of figure 3(b). These peaks are systematically blueshifted on increasing the growth temperatures of the lateral CdS. It should be noted that the \{2110\} top/bottom CdSe surfaces may have intrinsic structural defects. Since these defects offer nucleation sites, some of the CdS species may nucleate on these sites while others diffuse towards the \(\pm(0001)\) side surfaces. The incorporation of intrinsic CdS on the \(\pm(2110)\) surfaces results in the formation of non-uniform layer/islands, as indicated in the TEM image of figure 2(b). Parts of these CdS layers/islands may intermix with the central CdSe region. Therefore, based on the \(\mu\)-PL observations together with the TEM and EDS analyses, the central region may consist of non-uniform CdSSe covered with thin CdS layer/islands. Increasing the source temperature for lateral CdS growth will lead to a higher CdS vapor supply rate on the \(\pm(2110)\) surfaces. This effect leads to the central region being a more CdS-rich condition with increasing lateral CdS growth temperature, and in turn is responsible for the blueshift of the PL peaks. Another possibility may be considered. That is, the variation of the sulfur composition in the CdSe central region may be caused from the intermixing reaction of S/Se atoms. In addition, due to the large scales of all defects including thickness, width and length in CdS/CdSe lateral heterostructure NBs, the quantum confinement due to the size effect may not make a significant contribution to the spectral blueshift. Figure 3(b) shows the full width at half-maximum (FWHM) of the PL peaks as a function of emission wavelength for the heterostructure NBs. Even within the same sample, individual NBs show some statistical fluctuations in PL FWHM and peak position for CdSe-related peaks. Fluctuations in size, morphology, mole fraction, etc, within the same sample are commonly observed in NBs/nanowires grown by physical vapor transport [19]. This is due to local variation in growth temperatures or gas flow dynamics. The FWHMs of the lateral CdS peak for all samples are only 20 nm, reflecting high crystalline quality. However, the general trend in figure 3(b) shows that the FWHM from the central region increases with the blueshift in PL peak position. Thus the degree of non-uniformity in alloy composition of the central region may increase and results in the increase of FWHM of the PL spectra.

As mentioned earlier, the S mole fraction \(x\) and the morphology of CdS\(_{x}\)Se\(_{1-x}\) ternary NBs are closely related [13, 20]. Therefore, with increasing growth temperature, the VS growth mechanism is more dominant than the VLS mechanism and the incorporation of S is suppressed. However, in this CdS/CdSe lateral heterostructure NB, the S mole fraction and geometrical morphology are independent variables. Therefore, it is possible to control the mole fraction of the central NB region while keeping the morphology of NBs. In addition, CdS/CdSe lateral heterostructure NBs can be applied to many novel devices since the lower bandgap CdSe is surrounded by higher bandgap CdS. Furthermore, the lateral CdS structure may passivate the CdSe side walls which have a large number of non-radiative recombination centers. Therefore, this could be an ideal structure for a waveguide and laser medium with low propagation loss.

4. Conclusions

We have fabricated CdS/CdSe lateral heterostructure NBs via a two-step physical vapor transport method. Central CdSe NBs with lateral CdS structures were formed with the atomically
sharp interface. The large growth rate difference between CdS lateral structures at the ±(0001) side surfaces was found. This growth anisotropy has been attributed to the polar nature of the ±(0001) side surfaces. In addition, we observed that the surface diffusion of CdS species on the central CdSe region plays an important role in determining the shape of lateral CdS structures during the second growth step. The central CdSe region was covered with non-uniform CdS layers/islands which most likely nucleated on intrinsic structural defects of [2110] surfaces. The systematic blueshift of the μ-PL emission energy of the central region with the increase of growth temperature of the CdS lateral structure was observed. The novel structure and optical properties of these NBs allows the independent control of both the geometrical dimension and emission wavelength, which is advantageous for device applications.

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References