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Chinkyo Kim, Won Il Park, Gyu-Chul Yi, and Miyoung Kim

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Formation and photoluminescent properties of embedded ZnO quantum dots in ZnO/ZnMgO multiple-quantum-well-structured nanorods

Chinkyoo Kim  
Department of Physics, Kyunghee University, 1 Hoegi-dong Dongdaemun-gu, Seoul 130-701, Korea  
and Research Institute of Basic Sciences, Kyunghee University, 1 Hoegi-dong Dongdaemun-gu, Seoul 130-701, Korea

Won Il Park and Gyu-Chul Yi  
National CRI Center for Semiconductor Nanorods, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea and Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

Miyoung Kim  
School of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

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ZnO/Zn$_{0.8}$Mg$_{0.2}$O multiple-quantum-well (MQW) nanorods with a different number of periods and well widths were grown by catalyst-free metal-organic vapor phase epitaxy. Their optical and structural characteristics were investigated using photoluminescence, transmission electron microscopy, and field emission scanning electron microscopy. Unlike ZnO/ZnMgO MQW thin films, it was observed that embedded quantum dots played a more important role in the optical characteristics of ZnO/ZnMgO MQW nanorods than quantum confined Stark effect due to polarization field. © 2006 American Institute of Physics. [DOI: 10.1063/1.2352724]

The optical characteristics of semiconductor bulk materials are mainly determined by the inherent band structure of the material, but utilization of quantum well structures restricts carrier motion to quasi-two-dimensions and the confinement of carriers at the nanometer scale gives rise to various quantum effects on optical characteristics. Further reduction of dimensionality can be achieved through quantum dots (QDs). QD formation has the advantage of higher radiative recombination due to additionally formed density of states, which results in decreasing the lasing threshold, improving thermal stability, and exhibiting a narrow spectral line shape. Due to these advantages in optoelectronic device applications, many attempts have been made to fabricate QD structures with various semiconductors. It is very common to grow QD structures in strained thin films in a self-assembled way, but quantum dot formation in semiconductor nanowires and nanorods has not been reported, although many heterostructured nanowires and nanorods with well defined interfaces have been demonstrated. 1–3 It has been suggested that highly lattice-mismatched epitaxial layers for heterostructured nanomaterials could be grown without introducing misfit dislocations at the interface in nanorods. The reason for this intriguing feature was partly attributed to presumably efficient strain relaxation due to the proximity to open side surfaces in nanorods. 3,4 However, we recently showed that dislocations can be formed for GaN/ZnO coaxial nanorod heterostructures with small lattice mismatch. 5

As a candidate material for short-wavelength optoelectronic device applications, ZnO has drawn much attention due to its large excitonic binding energy of 60 meV and high thermal and mechanical stabilities. We recently investigated optical properties of ZnO/ZnMgO quantum structures 6–9 and observed an additional photoluminescence (PL) peak for the multiple-quantum-well (MQW)-structured nanorods with a thick well layer width in addition to a systematic blueshift of the dominant PL peak due to the confined state in the quantum wells. 9 However, the origin of the additional PL peak was not thoroughly investigated. Meanwhile, as for PL characteristics of ZnO/ZnMgO MQW structured thin films, similarly, Makino et al. previously reported the observation of an additional PL peak from the PL spectra of MQW-structured thin films with thicker quantum well width or higher Mg concentration. The additional peak was attributed to the transitions of spatially separated electron-hole pairs invoked by the quantum confined Stark (QCS) effect, which was induced by polarization field. 10 In contrast to the MQW thin films, however, the additional peak observed in MQW-structured nanorods turns out to be due to embedded QD. This implies that the strain is not fully relaxed in ZnO/ZnMgO nanorods and that efficient relaxation in the nanometer-scale area is not a universal characteristic of heterostructured nanorods. Here we report the observation of embedded quantum dot formation in ZnO/ZnMgO MQW-structured nanorods, which has a strong dependence on QW width and period.

ZnO/Zn$_{0.8}$Mg$_{0.2}$O MQW-structured nanorods were fabricated on c-plane sapphire substrates using metal-organic vapor phase epitaxy without employing metal catalyst. 11 In comparison with the catalyst-assisted nanostructure growth using the condensation-precipitation process through a metal catalyst, 1,2 this nanorod growth technique utilizes heteroepitaxial growth on the top surfaces of nanorods, which is a direct layer-by-layer growth mode, enabling easy control of both well width and composition. Using catalyst-free vapor phase epitaxy, ZnO/ZnMgO quantum well nanorods with subnanometer thick well layers can be grown. The schematic diagram and details of MQW-structured nanorod growth have been reported elsewhere. 9 In this work, the width ($L_w$) of ZnO well layers was varied from 11 to 44 Å while that of

4Author to whom correspondence should be addressed; electronic mail: gcyi@postech.ac.kr
ZnMgO barrier layers was fixed at 35 Å. The average concentration of Mg in the ZnMgO layers determined by energy dispersive x-ray spectroscopy in a transmission electron microscopy (TEM) chamber was about 20 at.%. Their optical and structural characteristics were investigated using PL, TEM, and field emission scanning electron microscopy (SEM). For PL measurements, a He–Cd laser (325 nm) was used as an excitation source and a He displex cooling system was employed to control sample temperature. Details of the PL measurements have been reported elsewhere.

Shown in Figs. 1(a) and 1(b) are the TEM images of ZnMgO/ZnO quantum well nanorods with $L_w$ of 11 and 44 Å, respectively. The dark and bright layers in these images correspond to ZnO and Zn$_{0.8}$Mg$_{0.2}$O layers, respectively. It is noted that the distinctive feature of the overall morphology of ZnO well layers is clearly shown for two samples. The sample with 11 Å [Fig. 1(a)] has uniformly thick disklike layers, while the sample with 44 Å [Fig. 1(b)] exhibits the truncated pyramid shape on a disklike plate. As shown in Fig. 1(b), two or three QDs are formed in the top part of the nanorod. From these TEM images, it is clear that the growth mode transition from quasi-two-dimensional islands or QD structures took place between 11 and 44 Å.

Schematic diagrams of two different well layer structures and related interband transition energy are illustrated in Fig. 1(c). In the case of MQWs with uniformly thin ZnO well layers, a unique interband transition state exists [Fig. 1(c)]. On the other hand, the excitons localized at the fringes of the well layers have the higher transition energy due to narrower thickness of $d_1$, while those at the truncated pyramids with the thickness of $d_2$ exhibit the lower transition energy [Fig. 1(c)]. Thus, it can be expected that the band edge emission consists of two components; one from the excitonic contribution in MQWs and the other from QD structure, which is what we have observed and will be explained in the following in detail. Previously, similar behavior of PL peak splitting has been reported in MgS/CdSe single-quantum-well structure where QW to QD transition occurs.

Figure 2 shows the low temperature PL spectra for the samples with one, four, seven, and ten periods of ZnO/Zn$_{0.8}$Mg$_{0.2}$O QW structured nanorods. Two plan view, SEM images of nanorod tips are also shown for the samples with a single QW and ten QWs, respectively. SEM images show that the tip morphology is well flat for the sample with a single QW, but not for the sample with ten QWs. The SEM images exhibit the truncated pyramid shape across the nanorod and relative height of transition energy. The dark and bright layers in these images correspond to ZnO and Zn$_{0.8}$Mg$_{0.2}$O layers, respectively. The distinctive feature of the overall morphology of ZnO well layers is clearly shown for two samples. The sample with 11 Å [Fig. 1(a)] has uniformly thick disklike layers, while the sample with 44 Å [Fig. 1(b)] exhibits the truncated pyramid shape on a disklike plate. As shown in Fig. 1(b), two or three QDs are formed in the top part of the nanorod. From these TEM images, it is clear that the growth mode transition from quasi-two-dimensional plates to three-dimensional (3D) island or QD structures took place between 11 and 44 Å.

Schematic diagrams of two different well layer structures and related interband transition energy are illustrated in Fig. 1(c). In the case of MQWs with uniformly thin ZnO well layers, a unique interband transition state exists [Fig. 1(c)]. On the other hand, the excitons localized at the fringes of the well layers have the higher transition energy due to narrower thickness of $d_1$, while those at the truncated pyramids with the thickness of $d_2$ exhibit the lower transition energy [Fig. 1(c)]. Thus, it can be expected that the band edge emission consists of two components; one from the excitonic contribution in MQWs and the other from QD structure, which is what we have observed and will be explained in the following in detail. Previously, similar behavior of PL peak splitting has been reported in MgS/CdSe single-quantum-well structure where QW to QD transition occurs. As the well width was increased further, the PL emission energies of $I_q$ and $I_{QD}$ decrease slightly.
Previously, the acceptor-bound excitons were reported to play an important role in PL spectra of freestanding ZnO QD structures due to a large number of acceptors resulting from an increased ratio of surface to volume.\textsuperscript{16,17} The absence of acceptor-bound exciton peaks in our samples, however, shows that the embedded QDs have different PL characteristics from that of freestanding QDs and demonstrates another route to acceptor-free ZnO QD application.

In conclusion, a series of ZnO/Zn$_{0.8}$Mg$_{0.2}$O MQW-structured nanorods with different well widths and periods has been fabricated on the top surfaces of the nanorods using catalyst-free vapor phase epitaxy. Embedded QD formation was observed from highly strained nanorods. In low-temperature PL spectra, clear emission peak splitting caused by the different electronic transition states was observed. The origin of the PL peak splitting was attributed to the growth mode transition from layer by layer to 3D island or QD structures, as observed in TEM and SEM. This implies that in ZnO/ZnMgO MQW-structured nanorods the growth mode experiences transition from layer by layer to island mode easily under strain and that as a consequence the QD effect is more dominant than the QCS effect induced by a strain-induced polarization field. For other semiconductor nanostructures not fully relaxed strain may also play an important role in both structural and optical characteristics.

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