

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

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ZnO/Zn<sub>0.8</sub>Mg<sub>0.2</sub>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.<sup>1–3</sup> 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.<sup>3,4</sup> However, we recently showed that dislocations can be formed for GaN/ZnO coaxial nanorod heterostructures with small lattice mismatch.<sup>5</sup>

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 nanorod quantum structures<sup>6–9</sup> 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.<sup>9</sup> 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.<sup>10</sup> 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<sub>0.8</sub>Mg<sub>0.2</sub>O MQW-structured nanorods were fabricated on *c*-plane sapphire substrates using metal-organic vapor phase epitaxy without employing metal catalyst.<sup>11</sup> In comparison with the catalyst-assisted nanostructure growth using the condensation-precipitation process through a metal catalyst,<sup>1,2</sup> 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.<sup>9</sup> In this work, the width ( $L_w$ ) of ZnO well layers was varied from 11 to 44 Å while that of

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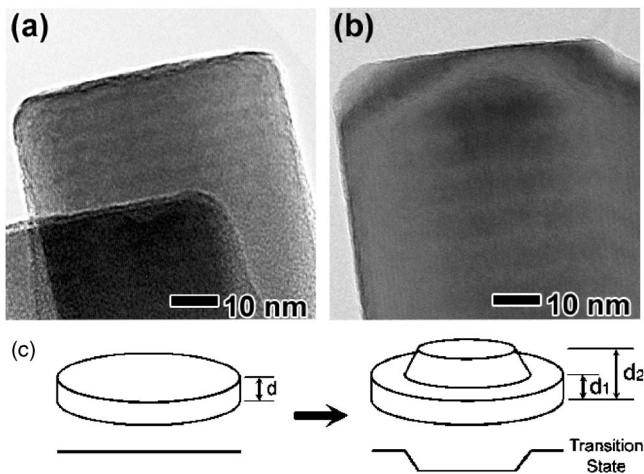


FIG. 1. (a) TEM image of ZnO/ZnMgO MQW-structured nanorods with  $L_w=11$  Å. (b) TEM image of ZnO/ZnMgO MQW-structured nanorods with  $L_w=44$  Å. Note that a quantum-dot-like structure is only observed in the sample with  $L_w=44$  Å. (c) Schematic diagrams of ZnO quantum well layer shape across the nanorod and relative height of transition energy.

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 displax cooling system was employed to control sample temperature. Details of the PL measurements have been reported elsewhere.<sup>12</sup>

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  $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{O}$  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.<sup>13</sup> 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.<sup>14</sup>

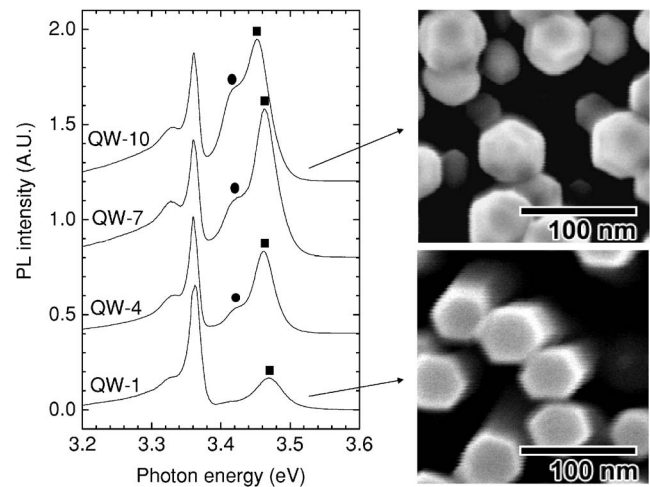


FIG. 2. Low temperature (measured at 10 K) PL spectra of ZnO/ $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{O}$  MQW-structured nanorods with different periods. SEM images show the morphology at the tip of nanorods.

Figure 2 shows the low temperature PL spectra for the samples with one, four, seven, and ten periods of ZnO/ $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{O}$  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. The SEM images show that the tip morphology is flat for the sample with a single QW, but not for the sample with ten QWs. From the TEM images in Fig. 1, this nonflat SEM morphology can be directly associated with QD formation. In PL spectra, a peak at 3.42 eV, which is attributed to radiative transition in QD, starts to appear from the four-QW sample. (The origins of other peaks will be discussed in the next paragraph.) From the PL spectra and SEM images, we can infer that QD formation does not take place for a single-quantum-well sample. The selective formation of QD only in MQW samples can be understood in terms of accumulated effect of strain field from each quantum well layer. For a single quantum well, the strain field was not large enough to create a QD.

Figure 3 shows the low temperature (measured at 10 K) PL spectra of ZnO/ $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{O}$  MQW-structured nanorods with different well widths. Three different groups of peaks are observed. The peak positions of the first group (denoted by  $I_{\text{ZnO}}$  in the following) did not change with well width. These peaks are attributed to neutral-donor bound excitons and their excited states (which are not clearly resolved in this spectra) in ZnO stem nanorods, which were consistently observed from PL spectra of pure ZnO nanorods and thin films.<sup>12,15</sup> The peak positions of a second group (denoted by  $I_{\text{QW}}$  in the following) shifted to lower energy as the well width was increased. These peaks are attributed to emission from MQWs and the well-width-dependent peak shift is due to the quantum confinement effect in ZnO/ $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{O}$  MQW-structured nanorods.<sup>9</sup> In addition to these two groups of peaks due to ZnO stem nanorods and MQWs, a third group of peaks (denoted by  $I_{\text{QD}}$  in the following) was observed for only the MQW-structured nanorods with well widths thicker than 25 Å.

For the MQW-structured nanorods with  $L_w=25$  Å,  $I_{\text{QD}}$  peaks start to appear at 3.411 eV, which occupied the lower energy side of  $I_{\text{QW}}$ . As the well width was increased further, the PL emission energies of  $I_{\text{QW}}$  and  $I_{\text{QD}}$  decrease slightly.

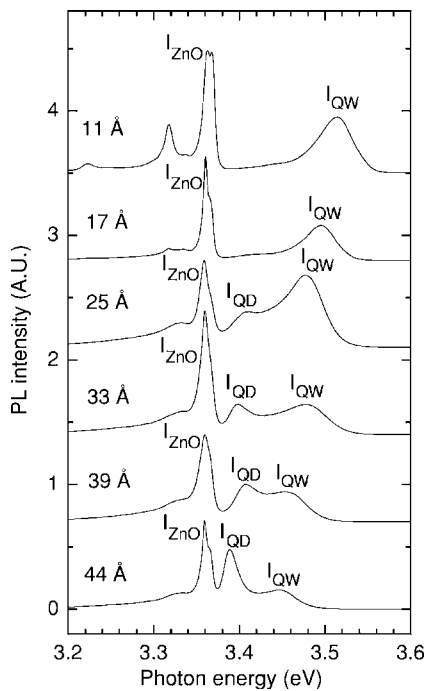


FIG. 3. Low temperature (measured at 10 K) PL spectra of ZnO/Zn<sub>0.8</sub>Mg<sub>0.2</sub>O MQW-structured nanorods with different well widths. Well-width-dependent peak positions of emission peaks marked by  $I_{QW}$  and  $I_{QD}$ .

The overall redshift of  $I_{QD}$  peak position can be understood by quantum confinement effect. The slight blueshift with the layer thicknesses from 33 to 39 Å may be due to the size fluctuation of QD within the layer. The similar behavior of nonmonotonic redshift of  $I_{QW}$  peak position is also shown and can be explained with the same argument. QD with lower energy states is expected to have more carriers per unit volume than QW. Thus, with the well layer thickness the luminescence from QD becomes more dominant than that of MQW. The relative ratio of integrated intensity of  $I_{QD}$  over peak  $I_{QW}$  increased drastically from 0.34 for a  $L_w$  of 25 Å to 3.1 for a  $L_w$  of 44 Å. That is, as  $L_w$  became thicker than 25 Å, additional exciton transition states corresponding to  $I_{QD}$  appeared and the density of these states increased with  $L_w$ . Apparently from our TEM and SEM measurements, these peaks correspond to radiative transition within QD structures.

The predominance of QD formation over the QCS effect in ZnO/ZnMgO nanorods can be understood in terms of strain relaxation. It was previously reported that unlike thin films, the strain due to lattice mismatch in nanorods is relieved within a few atomic layers from the interface.<sup>4</sup> Thus, the QCS effect invoked by polarization field in nanorods is relatively negligible. It should be, however, noted that the strain is not fully relaxed through the nanorods even though the extent of strain relaxation is large within a few atomic layers.<sup>4</sup> In other words, the unrelieved strain field propagates through the growth direction of nanorods and can cause QD formation when the accumulated strain from each layer of MQW structures is over a critical value.

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 resulted from an increased ratio of surface to volume.<sup>16,17</sup> 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<sub>0.8</sub>Mg<sub>0.2</sub>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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