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Evaluation of the discrete energy levels of individual ZnO nanorod single-quantum-well structures using near-field ultraviolet photoluminescence spectroscopy

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Spatially and spectrally resolved photoluminescence imaging of individual ZnO/ZnMgO nanorod single-quantum-well structures (SQWs) with a spatial resolution of 55 nm was performed using the optical near-field technique with a metallized UV fiber probe. Using excitation power density-dependent photoluminescence spectra of a ZnO/ZnMgO SQW nanorod, we observed the discrete energy levels in a ZnO quantum-well layer. © *2004 American Institute of Physics*.
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For future optical transmission systems with high data transmission rates and capacity, we have proposed nanometer-scale photonic devices (i.e., nanophotonic devices) and a method of integrating them.[1] These devices consist of nanometer-scale dots, and an optical near field is used as the signal carrier. As a representative device, a nanophotonic switch can be realized by controlling the dipole forbidden optical energy transfer among resonant energy level in nanometer-scale quantum dots via an optical near field.[2] It is made of sub-100-nm scale dots and wires, and their size and position on the substrate must be controlled with nanometer-scale accuracy. A nanometer-scale ZnO dot is a promising material for realizing these devices at room temperature, due to its large excition binding energy (60 meV).[3,4] Furthermore, the recent demonstration of semiconductor nanorod quantum-well structure enables us to fabricate nanometer-scale electronic and photonic devices on single nanorods.[5–8] Recently, ZnO/ZnMgO nanorod multiple-quantum-well structures (MQWs) were fabricated and the quantum confinement effect of the MQWs was successfully observed.[8] In addition, further improvement in the fabrication of nanorod heterostructures has resulted in the observation of significant photoluminescence (PL) intensity, even from nanorod single-quantum-well structures (SQWs).[9]

To confirm the promising optical properties of individual ZnO/ZnMgO SQWs for realizing nanophotonic devices, we measured the PL spectra using a low temperature near-field optical microscope (NOM). Using a metallized UV fiber probe, the spatial distribution of PL intensity and sharp PL spectra of individual ZnO well layers were observed.

$ZnO/Zn_{1-x}Mg_xO$ SQWs were fabricated on the ends of ZnO nanorods with a mean diameter of 40 nm using catalyst-free metalorganic vapor phase epitaxy.[8,10] The nanorods were grown on $Al_2O_3(0001)$ substrate. The average concentration of Mg (x) in the $Zn_{1-x}Mg_xO$ layers used in this study was determined to be $x=0.2$ using energy dispersive x-ray spectroscopy in a transmission electron microscopy chamber. The ZnO well layer thickness (L_w) investigated in this study was 2.5 nm, while the thicknesses of the $Zn_{0.8}Mg_{0.2}O$ bottom and top barrier layers in the SQWs were fixed at 60 and 18 nm, respectively (Fig. 1 shows a schematic diagram of the SQWs).

Figure 2(a) shows far-field PL spectra taken at 15 K at various excitation power densities. A strong, sharp peak (I_2)

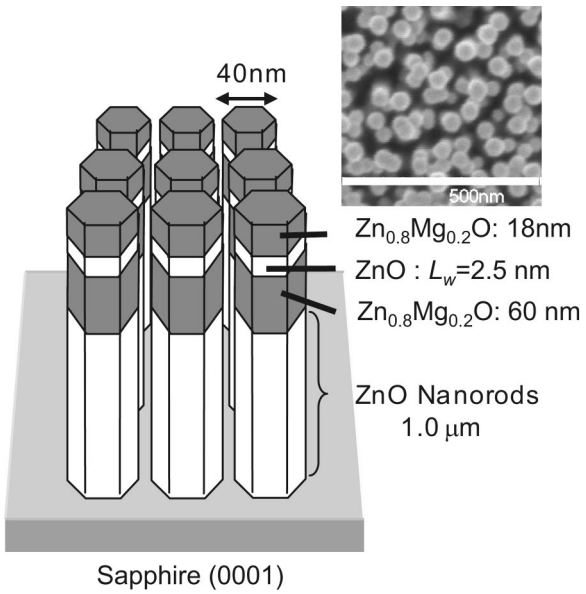

FIG. 1. Schematic of ZnO/ZnMgO SQWs on the ends of ZnO nanorods. The inset shows an overview of the ZnMgO/ZnO nanorod SQWs.

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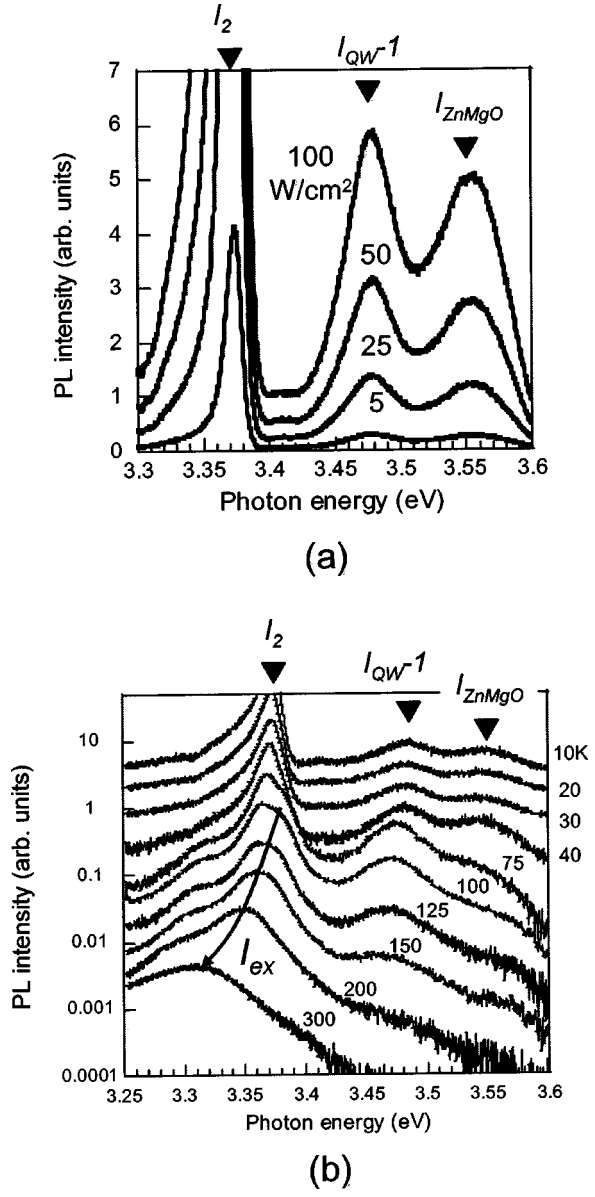

FIG. 2. (a) Power- (at 15 K) and (b) temperature-dependence of the far-field PL spectra of ZnO/ZnMgO nanorod SQWs.

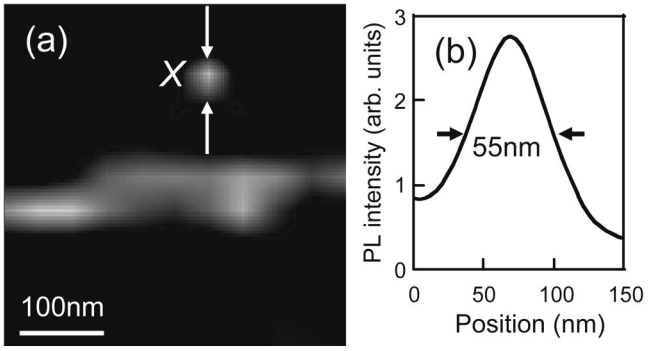

FIG. 3. Monochromatic PL image of ZnO/ZnMgO nanorod SQWs obtained at a photon energy of 3.483 eV. (b) Cross-sectional PL profile through spot *X*.

was observed at 3.371 eV, while broad peaks ($I_{QW}-1$ and I_{ZnMgO}) appeared at 3.480 and 3.555 eV. The number of peaks and their positions did not change up to 100 W/cm^2. Further experiments on the temperature-dependent evolution of the PL spectra in ZnO/$Zn_{0.8}Mg_{0.2}O$ nanorod SQWs confirmed the origin of the PL peaks. Figure 2(b) shows typical PL spectra of ZnO/$Zn_{0.8}Mg_{0.2}O$ nanorod SQWs measured over a temperature range from 10 to 293 K. At 10 K, a strong, sharp peak (I_2) was observed at 3.371 eV, while broad peaks appeared at 3.485 eV ($I_{QW}-1$) and 3.555 eV (I_{ZnMgO}). As the temperature increased, the intensities of the I_2 and I_{ZnMgO} peaks decreased drastically, and they almost disappeared at temperatures above 100 K, while the I_{ex} and $I_{QW}-1$ peaks increased relative to I_2 and I_{ZnMgO}. This behavior presumably results from the decomposition of bound excitons to free excitions owing to the increased thermal energy, and supports the argument described above, that PL I_{ex} and $I_{QW}-1$ peaks correspond to a free exciton peaks, and I_2 and I_{ZnMgO} are the well-known neutral-donor bound exciton peak emitted from ZnO nanorod stems and $Zn_{0.8}Mg_{0.2}O$ barrier layers, respectively. Furthermore, the $I_{QW}-1$ peak quenched rather slowly in comparison with the rapid quenching behavior of I_2. Slow thermal quenching is characteristic of quantum structures, supporting our postulate that I_{QW}-1 results from the quantum confinement effect. The experimental I_{QW}-1 peak energy was consistent with the theoretical value in a one-dimensional square potential well, in which $0.28m_0$ and $1.8m_0$ are the effective masses of electron and hole in ZnO, respectively, at a ratio of conduction and valance band offsets ($\Delta E_c/\Delta E_v$) of 9, and a band gap offset (ΔE_g) of 250 meV.

To examine the optical properties of individual ZnO/ZnMgO nanorod SQWs, we performed spatially and spectrally resolved PL spectroscopy using a low-temperature NOM system in illumination-collection mode.[11] A sharpened UV fiber probe with a 50-nm-thick aluminum film was used for the scanning. He–CD laser light ($\lambda = 325$ nm) was used to excite the ZnO/ZnMgO SQW through the UV fiber probe. The PL signal was collected with the same fiber probe as used for excitation, and detected using a cooled charge coupled device through a monochromator. The fiber probe was kept in close proximity to the sample surface ($\sim$10 nm) using the shear-force feedback technique.

Figure 3(a) shows the spatially and spectrally resolved PL image at 3.483 eV. Considering the rod diameter (40 nm), the bright spot labeled *X* [see Fig. 3(a)], the full width at half maximum of which was as small as 55 nm [see Fig. 3(b)], originated from one SQW nanorod. The spatial resolution, which almost equals the ZnO nanorod diameter, indicates that carrier tunneling between the nanorods can be neglected. Since the deep potential depth between the vacuum and the barrier layer is as much as 4 eV,[12] the carriers generated in the barrier layer in one nanorod are confined to the same nanorod through which the PL signal is collected. Furthermore, high spatial resolution imaging can be realized by enhancing the spatial resolution due to the plasmon resonance at the metallized sharpened tip.[13] Since the sharpened UV probe is entirely coated with a thin metal film, light propagates inside the fiber core and is efficiently converted into the surface plasmon mode at the metallic tip, just as with a Kretschmann configuration.[14] Such plasmon excitation effectively excites the carriers in the barrier layer and scatters the evanescent field of the ZnO quantum-well layer.

The five solid curves in Fig. 4(a) show the near-field PL spectra and their power dependence as determined by fixing the fiber probe at position *X* in Fig. 3(a). In the weak exci-

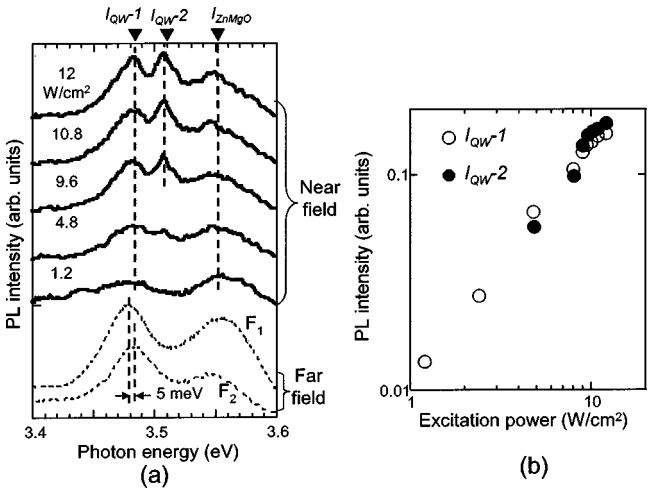

FIG. 4. (a) Solid curves show the near-field PL spectra of ZnO/ZnMgO nanorod SQWs at excitation densities ranging from 1.2 to 12 W/cm^2. The dashed curves (F_1 and F_2) show the far-field PL spectra. All the spectra were obtained at 15 K. (b) The excitation power dependence of the PL intensity at 3.483 (open circles) and 3.508 (closed circles) eV.

tation condition, a single PL peak is observed at 3.483 eV ($I_{QW}-1$). At excitation power densities exceeding 5 W/cm^2, another peak appears and grows at an energy of 3.508 eV ($I_{QW}-2$), which is 25 meV higher than $I_{QW}-1$. To confirm the origin of these emission lines, we plot the integrated PL intensity for the emission lines of both $I_{QW}-1$ and $I_{QW}-2$ in Fig. 4(b). The PL intensity of $I_{QW}-1$, indicated by the open circles, increases almost linearly up to 9 W/cm^2 and gradually saturates. This strongly implies that the $I_{QW}-1$ emission line originates from the recombination of the ground state, and the saturation suggests band-filling. As shown in the far-field spectra in Fig. 4(a) [see dashed curves F_1 and F_2], the energy difference at different positions was as small as 5 meV. Therefore, the large difference (25 meV) between $I_{QW}-1$ and $I_{QW}-2$ is not due to fluctuations in the ZnO well width. Furthermore, changing the temperature drastically alters the emission energy, as shown in Fig. 2(b); thermal heating due to the illumination light is absent. At a power density of around 6 W/cm^2, the PL line of $I_{QW}-2$ indicated by the closed circles appears. From this threshold-like PL behavior as a function of excitation power density, the PL line of $I_{QW}-2$ is associated with the emission of the first excited state. Considering the composition and size of the SQWs, the energy separation between $I_{QW}-1$ and $I_{QW}-2$ (25 meV) is in agreement with the prediction of the theoretical value of the energy difference ($\Delta E=E_{h2}-E_{h1}=21$ meV) between the first excited state of the hole (E_{h2}) and the ground state of the hole (E_{h1}). In this calculation, we used the following parameters: 0.28 m_0 and 1.8 m_0 for the effective masses of the electron and hole, respectively, and a band gap offset (ΔE_g) of 250 meV. This is the first detection of the excited state in ZnO quantum structures, although it has previously been observed in high-quality ZnO bulk crystals.[15]

In conclusion, we investigated the power-dependent features of individual ZnO/ZnMgO nanorod SQWs. Using a thin aluminum-coated UV fiber probe, we observed band-filing in the ground state and the resultant first excited state of a hole in ZnO/ZnMgO SQWs. This successful detection is attributed to the high spatial resolution (55 nm) of NOM and the high detection sensitivity utilizing plasmon resonance at the tip of the metallized UV fiber probe. The results shown here provide one criterion for realizing nanophotonic devices, such as the switching devices confirmed by the authors in CuCl quantum cubes.[2]

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[1]M. Ohtsu, K. Kobayashi, T. Kawazoe, S. Sangu, and T. Yatsui, IEEE J. Sel. Top. Quantum Electron. **8**, 839 (2002).
[2]T. Kawazoe, K. Kobayashi, S. Sangu, and M. Ohtsu, Appl. Phys. Lett. **82**, 2957 (2003).
[3]A. Ohtomo, K. Tamura, M. Kawasaki, T. Makino, Y. Segawa, Z. K. Tang, G. K. L. Wong, Y. Matsumoto, and H. Koinuma, Appl. Phys. Lett. **77**, 2204 (2000).
[4]M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science **292**, 1897 (2001).
[5]Y. Wu, R. Fan, and P. Yang, Nano Lett. **2**, 83 (2002).
[6]M. T. Björk, B. J. Ohlsson, C. Thelander, A. I. Persson, K. Deppert, L. R. Wallenberg, and L. Samuelson, Appl. Phys. Lett. **81**, 4458 (2002).
[7]M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith, and C. M. Lieber, Nature (London) **415**, 617 (2002).
[8]W. I. Park, G.-C. Yi, M. Kim, and S. J. Pennycook, Adv. Mater. (Weinheim, Ger.) **15**, 526 (2003).
[9]W. I. Park, S. J. An, G.-C. Yi, S. Hong, T. Joo, and H. M. Cheong, Appl. Phys. Lett. (in press).
[10]W. I. Park, D. H. Kim, S.-W. Jung, and G.-C. Yi, Appl. Phys. Lett. **80**, 4232 (2002).
[11]T. Saiki and K. Matsuda, Appl. Phys. Lett. **74**, 2773 (1999).
[12]M. W. Wang, J. O. McCaldin, J. F. Swenberg, T. C. McGill, and R. J. Hauenstein, Appl. Phys. Lett. **66**, 1974 (1995).
[13]T. Yatsui, K. Itsumi, M. Kourogi, and M. Ohtsu, Appl. Phys. Lett. **80**, 2257 (2002).
[14]*Surface Plasmons*, edited by H. Raether (Springer, Berlin, 1988).
[15]D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, G. Cantwell, and W. C. Harsch, Phys. Rev. B **60**, 2340 (1999).