ZnMgO quantum dots grown by low-pressure metal organic chemical vapor deposition

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The authors report on reproducible growth of ZnMgO quantum dots (QDs) by a metal organic chemical vapor deposition method. Mg is introduced into ZnO QDs, as confirmed by x-ray photoelectron spectroscopy and photoluminescence measurements. The size, density, and optical band gap of ZnMgO QDs can be well controlled by simply modulating the growth parameters.

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Due to numerous unique properties expected in the low-dimensional system, nanometer-scale materials promise to be important in the next-generation optoelectronic devices. Among versatile nanostructures, quantum dots (QDs) are of great interest because an ultimate quantum confinement can be established in QDs.¹ Consequently, considerable research efforts have been devoted to the QD system, including single-electron devices,^{2,3} core/shell structure,^{4,5} QD light emitting,^{6,7} and biological applications.^{8,9}

ZnO is presently receiving worldwide attention because of its advantages for blue/UV light emitters and detectors.^{10,11} Research activity on ZnO QDs has extensively increased over the past few years.^{12–16} In addition, doping—the intentional introduction of impurities—is fundamental to controlling the properties of semiconductors. It is known that the band gap of bulk ZnO can be tuned by alloying with MgO or CdO. Especially, the recent breakthrough in *p*-type doping bottleneck has made the potentials of ZnO materials more feasible.^{17–20} In these regards, similar efforts to dope ZnO QDs are strongly demanded. However, there have been few reports on this issue so far. In this letter, we develop a metal organic chemical vapor deposition (MOCVD) method to prepare ZnMgO QDs. The tailored properties of the QDs are readily presented.

QD samples were grown by a low-pressure MOCVD method. The substrates were *n*-type silicon wafers with 3° bias oriented from (111). Diethylzinc and O₂ were used as the zinc source and the oxygen source, respectively. N₂ was used as the carrier gas. Bis(cyclopentadienyl)magnesium (Cp₂Mg) and bis(methylcyclopentadienyl)magnesium [(MeCp)₂Mg] were used as the magnesium source. The growth temperature ranged from 350 to 450 °C. The chamber pressure was maintained at 6 Pa during the growth process. The crystal structures and morphologies of the ZnMgO QDs were characterized by x-ray diffraction (XRD) (Cu K α λ = 1.541 Å) and field-emission scanning electron microscopy (FE-SEM) (FEI Sirion 200 FEG). The chemical states of Mg were analyzed by x-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250, Al K α radiation source $h\nu$ = 1486.6 eV). Room-temperature photolumines-

cence (PL) measurements were performed using a He–Cd 325 nm laser as the excitation source. The electrical properties were examined by scanning tunneling microscopy (STM) (SPM Solver P47) at room temperature.

Figure 1 shows XRD pattern of the ZnMgO QDs grown at 400 °C. Only two peaks corresponding to ZnO (002) and Si (111) planes are observed, suggesting a total (002) preferential orientation for the ZnMgO QDs. The 34.4° (002) diffraction angle is in well agreement with ZnO bulk single crystal, implying that no evident residual stress or inclusion-induced lattice distortion due to Mg doping has developed during the growth process. According to the Debye-Scherrer method, the mean grain size of the QDs is calculated to be 10.2 nm.

Figure 2 illustrates FE-SEM top view images of the ZnMgO QDs grown at different temperatures. The QDs show an average diameter around 9 nm, which is consistent with the XRD results. As evident in the images, the density of the QDs is strongly temperature dependent. It decreases as the growth temperature increases, which can be explained in terms of the degree of supercooling. When the substrate temperature is low (e.g., 350 °C), the degree of supercooling is large. This results in a high density of nucleation center, and thus a high density of QDs is obtained, as shown in Fig. 2(a). Also, the opposite holds true for the high-temperature growth [e.g., 450 °C, Fig. 2(c)].

FIG. 1. XRD pattern of ZnMgO QDs grown at 400 °C.

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FIG. 2. FE-SEM top view images of ZnMgO QDs grown at different temperatures: (a) 350 °C, (b) 400 °C, and (c) 450 °C.

Another striking feature of the SEM images is that the average diameter of the QDs decreases with the increased temperature, especially in the case of high-temperature growth of 450 °C. This is because a self-assemble process can be influenced by the balance between adsorption and desorption of the reactive atoms. When the growth temperature is low, the process of adsorption is much more exquisite. Therefore, a high growth rate and a large diameter of the QDs are expected, as seen in Fig. 2(a). As the growth temperature increases, the balance between adsorption and desorption varies, which results in a low growth rate and corresponding small average diameter of the QDs [Fig. 2(c)]. It should be emphasized that the above-introduced dependence of the size and density of QDs on the growth temperature is not accidental and has been consistently repeated. These controllable characteristics are, therefore, well expected to offer better performance for the future devices based on ZnMgO QDs.

Much work has been reported on ZnMgO thin films.²¹ Also, quantum confinement has been observed in ZnO/ZnMgO nanorod heterostructures.²² Considering that a doping principle, applicable to bulk materials, may be quite different from a QD system,²³ Mg doping behavior, however, remains unclear in ZnO QD system. As a consequence, the chemical bonding states of Mg in ZnO QDs were examined by XPS. Figure 3 shows the Mg 1s narrow scan spectrum for the QDs grown at 400 °C. A peak around 1303.6 eV is observed, which is attributed to the Mg 1s core level. Thus, it is well confirmed that Mg is introduced into ZnO QDs.

In addition to XPS, PL measurements were performed to provide further evidence for the introduction of Mg. Figure 4 compares the PL spectra for the ZnO thin film, ZnO QDs,

FIG. 3. XPS narrow scan spectrum of Mg 1s region for ZnMgO QDs grown at 400 °C.

and ZnMgO QDs. ZnO thin film shows a dominant near-band-edge peak at 375.5 nm, which is attributed to a free exciton (FX) emission, whereas the FX emission of the ZnO QDs shows a blueshift to 372.6 nm, which is believed to be the result of quantum confinement effects. As expected, the FX emission of the ZnMgO QDs grown with Cp_2Mg source undergoes a further blueshift to 370.1 nm. Note that SEM and atomic force microscopy measurements reveal the same average diameter around 9 nm and height around 6 nm for the ZnMgO and ZnO QDs (data not shown). It is, therefore, inferred that both quantum confinement effects and Mg doping contribute to the band gap widening simultaneously in our ZnMgO QDs. Furthermore, the FX emission shifts to 366.8 nm for the ZnMgO QDs grown with $(\text{MeCp})_2\text{Mg}$ source. This further blueshift is associated with the increased Mg content because the $(\text{MeCp})_2\text{Mg}$ source possesses a higher vapor pressure in comparison with Cp_2Mg . This inference is also supported by the fact that the Mg content in these two ZnMgO QDs are 1.1% and 2.3%, respectively, obtained from XPS measurements. The comparative PL spectra suggest that the Mg content can be tuned and a tailored optical band gap is achieved for the ZnMgO QDs.

Finally, the effects of Mg incorporation on electrical properties of ZnMgO QDs were characterized by STM. The tip of the probe contacted directly with the QD, eliminating any tunnel current. Figure 5 illustrates the current-voltage

FIG. 4. Comparative room-temperature PL spectra for ZnO thin film, ZnO QDs, and ZnMgO QDs grown at 400 °C.

FIG. 5. STM I - V characteristics of ZnO and ZnMgO QDs grown at 400 °C.

(I - V) characteristics of the ZnO and ZnMgO QDs grown at 400 °C. The nonlinear I - V characteristic for the both samples indicates a barrier between the tip and QDs, which is probably associated with the native defects in QDs.²⁴ The current of the ZnMgO, however, is always smaller than that of ZnO. It is possible that the Mg incorporation increases the barrier height for the ZnMgO QDs. Also, there is a possibility that the addition of Mg moves the conduction band edge up in energy and potentially away from the intrinsic shallow donor state.²⁵ Correspondingly, an increase in activation energy of the defect donors and resistivity of the QDs is expected for the ZnMgO QDs.

In summary, we have demonstrated reproducible growth of ZnMgO QDs by a MOCVD method. The size, density, and optical band gap of the QDs can be well controlled by simply modulating the growth parameters. In addition, an evident change in QD transport properties due to introduction of Mg is observed. Considering all the tunable characteristics and the standard MOCVD technology, incorporating ZnMgO QDs into future optoelectronic devices deserves an eager expectation.

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