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Yu-Yun Peng, Tsung-Eong Hsieh, and Chia-Hung Hsu

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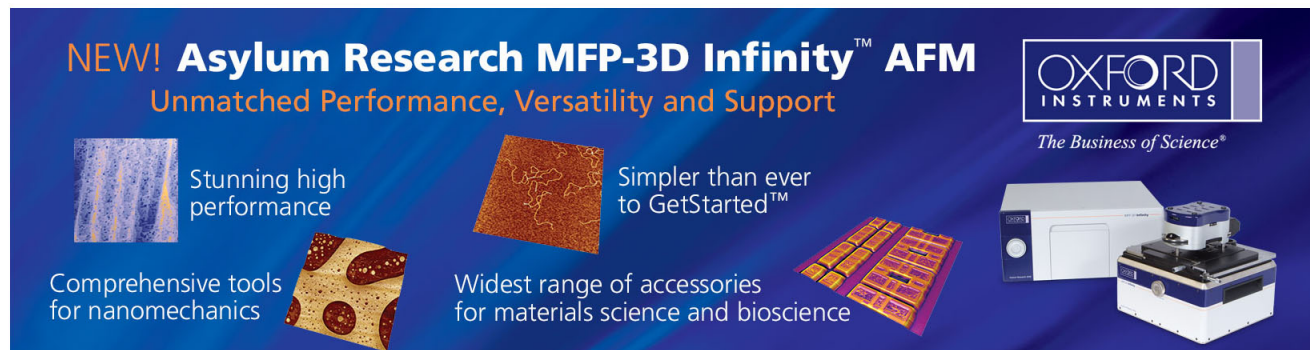
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Optical characteristics and microstructure of ZnO quantum dots-SiO₂ nanocomposite films prepared by sputtering methods

Yu-Yun Peng^{a)} and Tsung-Eong Hsieh^{b)}

Department of Materials Science and Engineering, National Chiao-Tung University, Hsinchu, Taiwan 300, Republic of China

Chia-Hung Hsu^{c)}

Research Division, National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu, Taiwan 300, Republic of China

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ZnO quantum dots (QDs)-SiO₂ nanocomposite films were prepared using the target-attached radio-frequency sputtering. The transmission electron microscopy revealed the uniform dispersion of ZnO QDs with diameters about 2–7 nm in amorphous SiO₂ matrix. The photoluminescence showed that small ZnO QDs are able to emit white light with luminescence spectra similar to those of the present GaN-based light emitting diode (LED). The calculated chromaticity coordinates of emitting light evidenced the feasibility of ZnO QDs-SiO₂ nanocomposite films as the fluorescence material in optoelectronic devices. © 2006 American Institute of Physics.

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In recent years, intrinsic properties of quantized materials have been explored and unique innovations in related fields were proposed. Among all nanosized substances, II-VI and III-V semiconductor quantum dots (QDs) are the most popular one in the field of optoelectronics.^{1–3} At present, chemical synthesis methods are the most common way to grow uniformly dispersed QDs. However, the QDs prepared by such methods are relatively unstable and encounter the difficulties in dispersion and preservation. Formation of core-shell structure and matrix passivation are commonly adopted to stabilize the QDs when coupling with devices. Recently, the surface chemistry methods by immersing the semiconductor QDs in polymer^{4,5} or glass^{6,7} matrix to block the dangling bonds have attracted lots of attention. Distinct photoluminescence (PL) properties have been demonstrated lately in both QDs/polymer⁸ and QDs/glass⁹ systems that can serve as fluorescent materials or active media in tunable lasers to achieve full color emission.

Zinc oxide (ZnO) QD is another popular system widely studied in the past decade.^{10–16} ZnO is a wide-band-gap semiconductor ($E_g = 3.25\text{--}3.5$ eV) and its large exciton binding energy (59 meV) gives rise to the high efficiency exciton emission at room temperature.¹⁷ Processing methods such as sol-gel,^{18,19} molecular capping,^{20,21} etc.,^{22–24} have been employed to disperse ZnO nanoparticles in silica or polymeric matrix. It had been found that the defect structure and transition mechanisms could be modified by the amount and distribution of ZnO QDs in SiO₂ matrix to yield distinct luminescence properties.²⁵

In this work, ZnO QDs-SiO₂ nanocomposite films with dot diameter about 2–7 nm were prepared via target-attached radio-frequency magnetron sputtering method. High purity ZnO chips were placed on a 3 in. quartz target during sputtering to fabricate ZnO QDs-SiO₂ films. Si wafer was used as substrate. Sputtering was carried out with 50–300 W

at about 3–10 mtorr working pressure. During deposition, no substrate heating or postgrowth annealing was performed. The microstructure was characterized by transmission electron microscopy (TEM) (Philips TECNAI 20). The PL spectra were measured at room temperature using a 325 nm He-Cd laser.

Figure 1(a) shows TEM images of nanocomposite films containing different sizes of ZnO QDs. Images of several QDs after the complex image processing of autocorrelation²⁶ are presented in Fig. 1(b) in order to reveal the short-term periodic signals of the high-resolution transmission electron microscopy (HRTEM) images. These images evidence that the embedded ZnO QDs are in a form of nanocrystals rather than the amorphous clusters.

The PL spectra of ZnO QDs-SiO₂ nanocomposite films are shown in Fig. 2. By utilizing the Gaussian curve fitting, it was found that each of these spectra is composed of three emission bands located at violet, blue, and green-yellow regions.²⁵ When the dot diameter is smaller than 3 nm, the spectra are dominated by strong violet and blue emissions. As shown in Fig. 2(a), the shapes of the spectra and the luminescence intensities become similar to that of a blue GaN light emitting diode incorporating with yellow yttrium aluminum garnet phosphors. The relative intensity of the violet band declines rapidly when the dot sizes increase. With dot diameters larger than 6 nm, the blue emission gradually decreases and the strong green-yellow emission¹⁴ dominates the spectra as revealed by Fig. 2(b). The broad green-yellow emission resulted from recombination of electrons at the conduction band (CB) edge or exciton states with deeply trapped holes V'_0/V''_0 (2.0–2.2 eV below CB) in the bulk of ZnO QDs.^{11,27,28} The blue emission is attributed to the recombination of electrons with V'_{Zn} [about 0.7 eV above valence band (VB)] in the depletion region of ZnO QD surfaces.²⁵

Figure 3(a) presents the peak shift of the three emissions versus the sizes of ZnO QDs. The blueshift behavior is quite obvious when the dot diameters decrease from about 7 to 5 nm; however, it becomes obscure when the diameters

^{a)}Electronic mail: ppy.mse90g@nctu.edu.tw

^{b)}Electronic mail: tehsieh@cc.nctu.edu.tw

^{c)}Electronic mail: chsu@nsrrc.org.tw

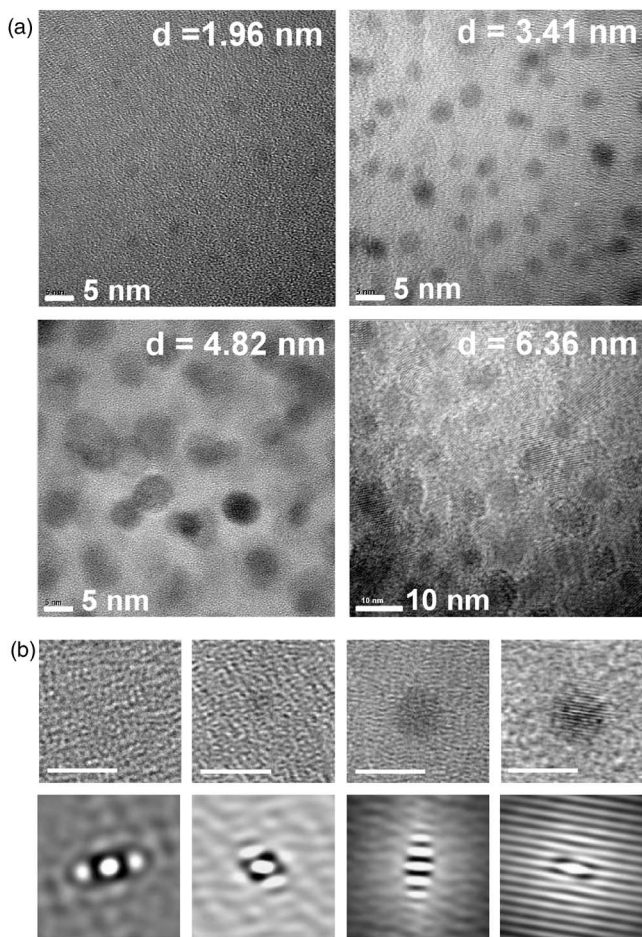


FIG. 1. (a) TEM images of ZnO QDs-SiO₂ nanocomposite thin films containing different dot diameters from 2 to 7 nm. (b) The figures in the upper row are HRTEM images of various ZnO QDs (the first image on the upper left-hand side is the amorphous SiO₂ matrix with no appreciable periodic signal). The lower-row figures are the images of ZnO QDs subjected to the autocorrelation processing. The white bold lines denote the scale bar of 5 nm in length.

are smaller than 5 nm. The bandwidths of emission bands versus the dot diameters are shown in Fig. 3(b) and it depicts a relatively small band broadening with the decrease of dot sizes. Different from the violet and blue emissions, the extremely broad bandwidth of the green-yellow emission was induced by the homogeneous broadening of the longitudinal-optical (LO) phonons.¹⁷ The slight rising of the violet bandwidth for dot sizes larger than 5 nm was attributed to the uncertainty of curve fitting that resulted from the gradual submergence to the tails of the blue and green-yellow emissions. The integrated intensity ratios of the three emissions in

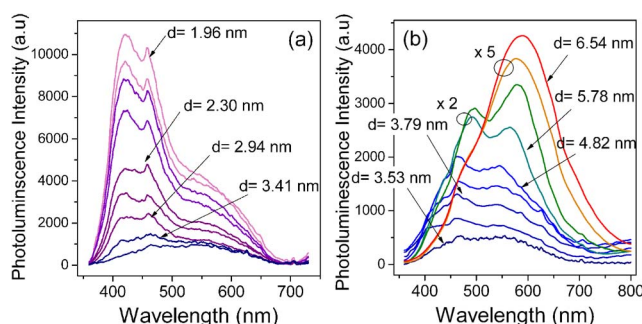


FIG. 2. (Color online) Photoluminescence spectra of ZnO QDs-SiO₂ films.

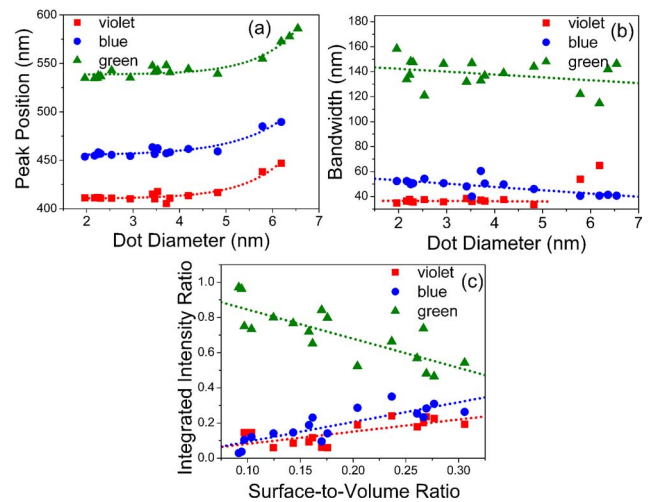


FIG. 3. (Color online) PL spectrum analysis by Gaussian curve fitting. The relations of (a) peak position, (b) bandwidth, and (c) integrated intensity ratio of individual emission bands are plotted vs the dot size and surface-to-volume ratio.

Fig. 3(c) show that the magnitudes of the violet and blue emissions increase with the increase of surface-to-volume ratio and vice versa for the green-yellow emission. Similar to the blue emission,²⁵ it was speculated that the violet emission should also originate from the depletion region at the surface of ZnO QDs. The mechanism for the violet emission correlated to surface-bound impurities²⁹ or donor-acceptor pair^{13,17,27,30} at the dot surface has been identified. However, in this work the matrix for the embedded ZnO QDs is different from those reported in previous studies.^{29,31,32} Present RT-PL data are insufficient to justify the QD/matrix interface effects on the mechanisms responsible to the violet emission and further study is required.

Dijken *et al.*¹⁴ identified the visible emission with the assumption that the energetic position of the deeply trapped hole is independent of dot size. However, in our cases, the trap levels did not depict a strong blueshift behavior as proposed in the work of Dijken *et al.*¹⁴ In the model of Dijken *et al.*,¹³ O_i''/O_i' at the surface are able to trap carriers and allow them to tunnel back into the particles. Consequently, both $V_O \leftrightarrow V_O'$ and $V_{Zn}'' \leftrightarrow V_{Zn}'$ transitions are affected by O_i''/O_i' ions. It is speculated that such a correlation in the O_i''/O_i' -rich ZnO QDs-SiO₂ system enables O_i''/O_i' ions to pin the traps and thus elevates the energetic positions of traps in a manner similar to the CB edge. In addition, the slight extension of the trapping band (the increase of the energy separation between the replica states of LO phonons) attributed to the compressive strain and large deformation for ZnO QDs embedded in the matrices also arises.³²⁻³⁵ Nevertheless, it was proposed that the LO-phonon frequency is a weak function of the sizes of nanoparticle³⁵ and such an argument agrees well with the result of the small variations of the bandwidth as presented in Fig. 3(b).

The calculated CIE chromaticity coordinates of the emitted light were presented in Fig. 4. The diagram reveals that the color chromaticity of light moves along a trajectory that originated from the violet region, passing through the white regions, and eventually resides in the yellow-light region. This evidences the feasibility of the ZnO QDs-SiO₂ films serving as a fluorescence material of optoelectronic devices.

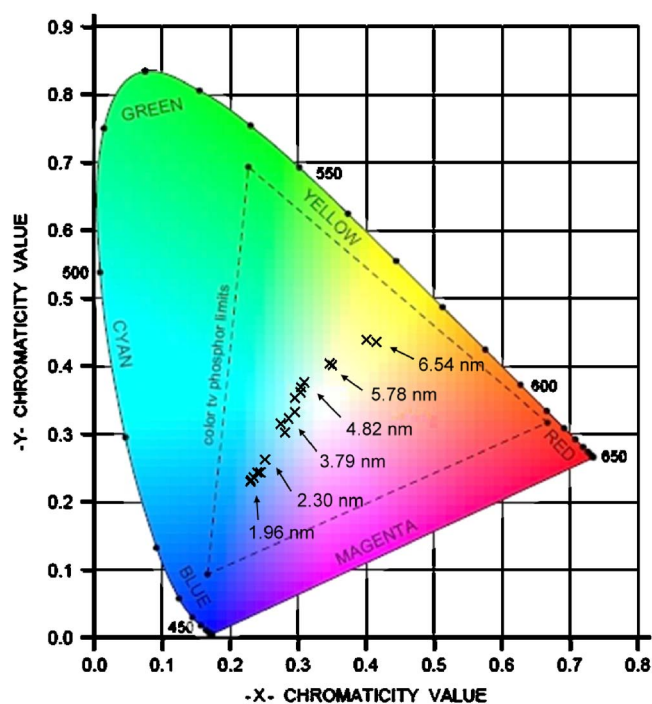


FIG. 4. (Color online) CIE chromaticity diagram of the ZnO QDs-SiO₂ films. The diameters of QDs are specified in the diagram.

In conclusion, we reported a simple method of fabricating ZnO QDs-SiO₂ nanocomposite thin films containing QDs of diameters from about 2 to 7 nm. The experiment showed that the defect structures experience the quantum confinement effect and are affected by the phonon interactions due to the change of strain status as the dot sizes decrease. The feasibility of ZnO QDs-SiO₂ nanocomposite films serving as the fluorescence material in optoelectronic devices was also demonstrated.

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