Self-assembled ZnO quantum dots with tunable optical properties

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Self-assembled ZnO quantum dots (QDs) were achieved by a vapor phase transport process. ZnO nanodots were naturally formed on solid substrates in the Volmer-Weber growth mode. Size control of nanodots could be readily realized by varying the growth time. The as-prepared ZnO QDs are of high quality and very stable after formation. The blueshift of band gap energies derived from quantum confinement effects was confirmed by optical absorption spectra. Photoluminescence spectra revealed the tunable behavior of ultraviolet luminescence due to exciton localization. The realization of size-tuned color from ZnO QDs makes them more promising for practical applications. © 2006 American Institute of Physics. [DOI: 10.1063/1.2221892]

Semiconductor quantum dots (QDs) are known for unique behaviors, having the size-tunable atomiclike properties arising from quantum confinement in the nanometer scale. II-VI semiconductor QDs such as CdSe and ZnSe,[1–3] as compared with IV and III-V materials,[4–6] have attracted more attention due to the higher exciton binding energies and stronger exciton-photon interactions in these materials. Unfortunately, the band gap of bulk CdSe is 1.74 eV, which is difficult to be tuned to ultraviolet (UV) range, and moreover it is toxic and cannot be easily used for human medical applications; ZnSe can be used in the UV-blue region, but its related devices are heavily degraded by the resulting defects. ZnO, having a wide direct band gap of 3.37 eV at room temperature, is a promising candidate for short-wavelength devices. Due to the large exciton binding energy of 60 meV, ZnO is known to be the brightest emitter of available wide-gap semiconductors.[7] In addition, ZnO has other significant attributes, such as high defect resistance, long-term stability, environmental friendliness, biosafeness and biocompatibility, and low material cost. In these regards, ZnO QDs gain the advantage over CdSe and ZnSe for practical applications.[8]

ZnO QDs or nanoparticles are prepared mainly by wet preparation methods.[9–12] These techniques require large amounts of solvents, multiple process steps, minute control on composition, as well as long processing times. The controlled growth is very difficult. Recently, the selective growth of ZnO QDs has been reported by a metal-organic chemical vapor deposition (MOCVD) technique on SiO_2/Si substrates.[13] More recently, we have developed a vapor phase transport (VPT) growth process to produce ZnO QDs directly on Si and such substrates.[14] The realization of ZnO QDs on conventional solid substrates gives us an opportunity to gain a fundamental understanding of this nanostructure. In this letter, we demonstrate that the VPT process allows the creation of self-assembly of ZnO QDs in the Volmer-Weber growth mode, with controllable nanodot sizes. The size-tuned optical properties were firmly identified by optical absorption and photoluminescence (PL) spectra.

ZnO QDs were synthesized by a VPT growth process under controlled conditions. Detailed growth process could be found elsewhere.[14] Briefly, ZnO QDs were synthesized by thermally evaporating zinc acetate powders at 500 °C with a 20% O_2/Ar mixture gas flow. The deposition time varied from 2 to 4 min. The products were collected on a substrate placed at a relatively low temperature for property examinations. The morphologies and structures of the products were investigated by a FEI Sirion 200 FEG field-emission scanning electron microscope (FE-SEM), a Philips CM200 transmission electron microscope (TEM), and a Bede D1 x-ray diffraction (XRD) system. The chemical composition was analyzed using an energy dispersive x-ray spectroscopy (EDX) attached to the SEM. PL measurements were performed at room temperature by using a He–Cd laser (325 nm) as the excitation source. Absorption was measured with a Lambda 20 UV-visible spectrometer.

Figure 1 illustrates the SEM micrographs of products collected on Si substrates with different growth durations. The images clearly identify the appearance of ZnO QDs, and essentially no obvious aggregation can be found. The formation of wurtzite ZnO nanocrystals was confirmed by EDX and XRD observations (not shown here), which are similar to those illustrated in our previous report.[14] Size control of ZnO QDs can be achieved simply by varying the growth time. The observed average nanodot diameters increase approximately from 10 to 15 to 21 nm as the growth time increases from 2 to 3 to 4 min, with their nanodot densities about on the same order of 10^{11} cm^{-2}. Almost the same results have been obtained on sapphire substrates.
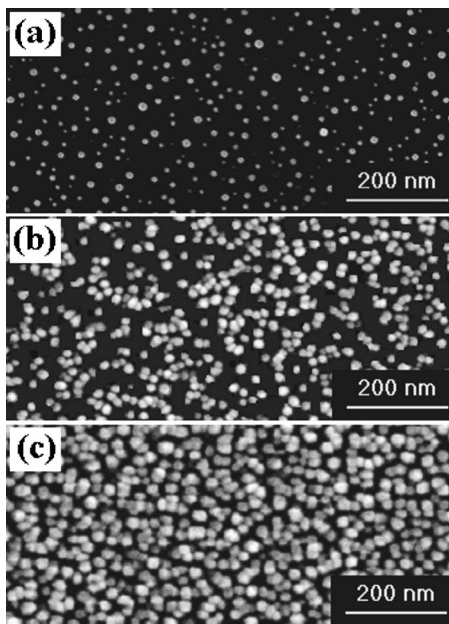
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FIG. 1. SEM images of as-prepared ZnO QDs with different growth times of (a) 2, (b) 3, and (c) 4 min.

FIG. 3. Dot dimension distribution of individual ZnO QDs determined by TEM measurements. The solid line is the slope obtained by the linear fitting of all the points. The parentheses indicate (average height, average diameter) in units of nanometers.

It should be noted that the nanodot diameter observed in SEM is within the base area of the dot, and so usually overestimated as compared with the most probable value obtained from analysis of the TEM images. Thus, to illustrate the morphology of ZnO QDs precisely, TEM measurements were performed on samples. Figure 2 shows the plan-view and cross-sectional TEM images of ZnO QDs deposited for 2 min as an example. The TEM observations, together with the SEM images shown above, serve to firmly establish the naturally direct growth of ZnO QDs on solid substrates. We demonstrate that ZnO QDs could be formed in the Volmer-Weber growth mode. The Volmer-Weber QDs or islands have been reported in such semiconductors as Si,[4] (In,Ga)As,[5] and ZnSe.[1] Thus, the realization of ZnO QDs in the Volmer-Weber growth mode as reported here can be expected to open a feasible avenue to study and create new forms of this material.
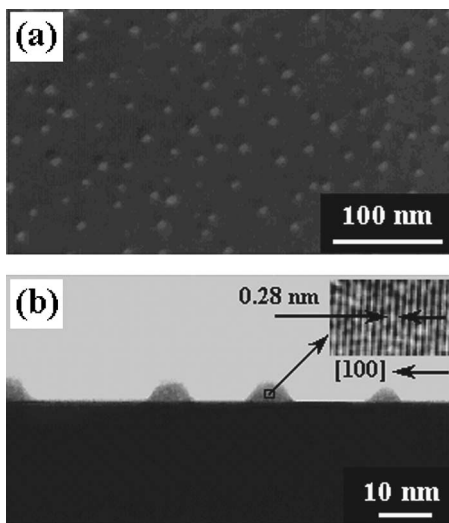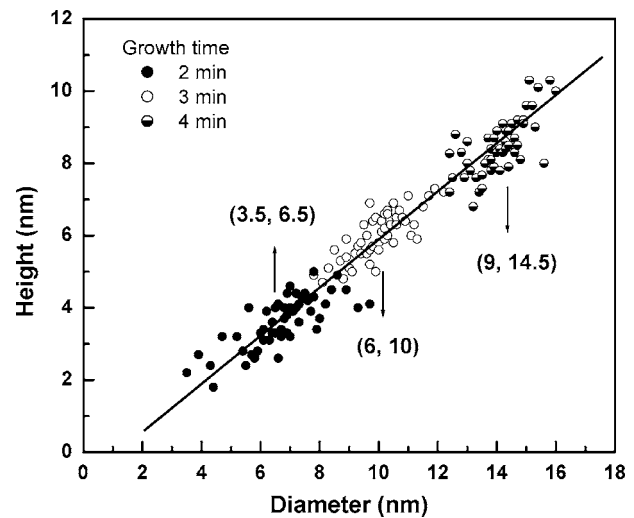

FIG. 2. (a) Plan-view and (b) cross-sectional TEM images of as-prepared ZnO QDs. An inset high-resolution TEM image shows that the ZnO QDs are single crystal. The growth time is 2 min.

The dimension distribution of individual QDs deduced from TEM measurements is plotted in Fig. 3. It is clear that the nanodot size becomes larger by the increase of the ZnO deposition, which is in accordance with the SEM observations. The nanodot dimensions increase from (3.5, 6.5) to (6, 10) to (9, 14.5) as the growth time is up from 2 to 3 to 4 min if the parentheses indicate (average height, average diameter) in units of nanometers. Although the average size of the dots varies with growth conditions, the distribution of sizes in any one growth is relatively narrow. The dot profile exhibits that the nanodot height is proportional to the diameter, with the height-to-diameter ratio consistently at about 1:1.8, independent of dot size, which is similar to that observed in III-V dots.[6] ZnO QDs obtained here are single crystal in nature as illustrated by the high-resolution TEM image in the inset of Fig. 2(b).

ZnO QDs smaller than about 7 nm in dimension exhibit a so-called quantum confinement effect, an enlargement of the band gap that is typically measured by the blueshift of light absorption. Figure 4 shows the normalized optical absorption spectra of the as-prepared ZnO QDs. The band gap energies thus determined from absorption spectra reveal the blueshift from 3.34 to 3.41 to 3.57 eV as the QD size decreases. Theoretically, the band gap of ZnO QDs can also be calculated from nanodot sizes based on the effective mass approximation.[15] By using the expression developed in Ref. 14, the calculated values are 3.36, 3.42, and 3.62 eV for ZnO QDs with the dimensions of (3.5, 6.5), (6, 10), and (9, 14.5), respectively. The theoretical values are consistent with the experimental data, but always with a deviation towards larger values, which is believed to be the results of the use of an infinitely high barrier potential with vanishing wave functions at the boundaries of the equation. Regardless of the discrepancy, the results firmly demonstrate that the band gap of ZnO QDs shifts to higher energies as the nanodot size decreases. Nanocrystals larger than 7 nm in height do not show any blueshift and have a band gap close to that of bulk ZnO (3.37 eV). On the contrary, ZnO QDs with the dimension of (3.5, 6.5) show an energy ~3.57 eV, much larger than the band gap of bulk ZnO. Since the QD structures studied in this work are open structures and the QD surfaces
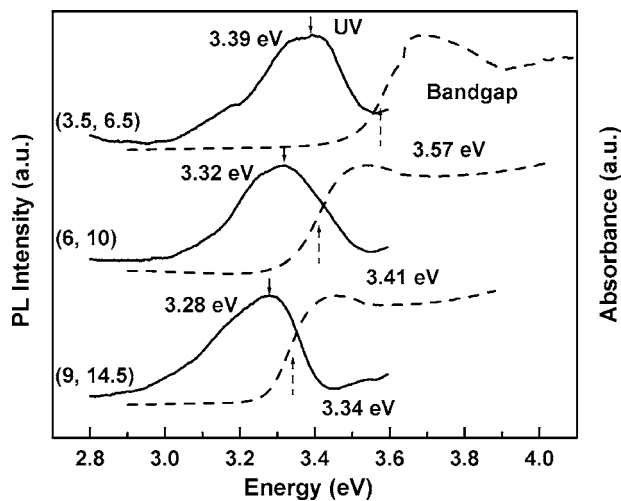
FIG. 4. Room-temperature optical absorption (dashed line) and PL (solid line) spectra of as-prepared ZnO QDs. The dashed arrows show the band gap of ZnO QDs determined by the derivative of absorption curves. The solid arrows show the UV emission from ZnO QDs. The parentheses indicate the nanodot dimensions.

are under the stress free condition, the strain-induced band gap shift should not be taken into account. Accordingly, it is very reasonable to attribute this blueshift of the band gap of ZnO QDs with increasing dot sizes due to the quantum confinement effects.

Figure 4 also shows the normalized global room-temperature PL spectra of the as-prepared ZnO QDs with different average sizes. The ultraviolet (UV) emission occurs in ZnO QDs and shifts to higher energies (from 3.28 to 3.32 to 3.39 eV) as the nanodot dimension decreases. This blueshift behavior of PL peak position is naturally explained by the expected effect of quantum confinement as discussed above. In general, quantum confinement shifts the energy levels of the conduction and valence bands apart, giving rise to a blueshift in the transition energy as the nanodot size decreases. The UV luminescence is believed to come from bound or localized excitons in ZnO QDs.[16] It is well known that the exciton localization is so strong in ZnO QDs that it can manifest itself even at room temperature.[16,17] As clearly identified in Fig. 4, by varying the nanodot size, the room-temperature luminescence in the UV region can be readily tuned from 3.28 to 3.39 eV for ZnO QDs obtained here. This size-dependent emission wavelength manipulation indicates that this material system may be an ideal candidate for use in tunable emitters for biomedical labels, light emitting diodes (LEDs), lasers diodes (LDs), and sensors.

In Fig. 4 the Stokes shift can be observed as an indicator of the exciton localization in ZnO QDs. The Stokes shift becomes larger (from 60 to 90 to 180 meV) as the nanodot size decreases, suggesting the enhancement of the degree of exciton localization. The exciton localization can effectively annihilate the nonradiative recombination centers, thereby having a significant effect on the device performance such as determining the emission energy in LEDs and contributing to luminescent efficiency and optical gain within laser structures.[16,17] In addition, the dead layer could be formed near the QD surface with the thickness up to 1.6 nm due to the specific dielectric constants and effective masses of hole and electron in ZnO.[18] The rather thick dead layer in ZnO

QDs is expected to further improve luminescence owing to the exciton separation from the surface defects. These characteristics make ZnO QDs very promising for optoelectronic applications.

Previous studies on CdSe and ZnSe QDs revealed that they could be unstable in some cases.[2] To clarify the stability of ZnO QDs, we evaluated them at intervals after deposition. No change in the SEM images was observed for all the samples, and moreover there was almost no difference appeared in the optical absorption and PL spectra, both position and shape, even after being aged over 15 months. The samples were kept in an ordinary silica-gel desiccator under atmospheric conditions. These observations indicate that the ZnO nanodot structures and their characteristics are time independent; that is to say, ZnO QDs are very stable as expected. The results presented here strongly suggest that ZnO QDs should be more suitable for the practical short-wavelength applications as compared with CdSe and ZnSe QDs.

In summary, we have realized self-assembled ZnO QDs on solid substrates by a VPT process in the Volmer-Weber growth mode. The nanodot sizes could be readily controlled by varying the growth durations. The color-tunable nature of QDs was unambiguously demonstrated by optical absorption and PL spectra in the ZnO system. The obtained ZnO QDs were of high quality and stability in their features. The recognition presented in this work opens the door for the creation, study, and application of ZnO QDs in a systematic and controlled manner.

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