

Behind the weak excitonic emission of ZnO quantum dots: ZnO/Zn(OH)₂ core-shell structure

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The structure of ZnO quantum dots prepared via the wet chemical method was studied. By introducing an annealing treatment (150 °C–500 °C), we also investigated the effect of the change in the structure of the dots on their luminescence properties. Our studies revealed that the surface of the as-prepared dots is passivated by a thin layer of Zn(OH)₂, thus, the dots consist of a ZnO/Zn(OH)₂ core-shell structure. We present evidence that the weak excitonic transition of ZnO quantum dots is strongly correlated with the presence of the surface shell of Zn(OH)₂. When Zn(OH)₂ is present, the excitonic transition is quenched. © 2002 American Institute of Physics. [DOI: 10.1063/1.1432763]

In the recent years, ZnO as a wide band gap semiconductor (energy gap of 3.35 eV at room temperature) has attracted considerable attention for the promising applications as ultraviolet (UV) light-emitting diodes and laser diodes. However, experiments so far showed that, compared with high quality ZnO single crystal films^{1,2} or the surface capped ZnO nanoparticles,^{3,4} the UV band gap luminescence in as-prepared ZnO quantum dots (QDs) is strongly quenched,^{5–7} and the broad oxygen-deficiency related⁸ green luminescent band is predominant. It was found that both the size⁵ and the surface^{3,4,9} of the dot have an effect on the luminescence properties. A better understanding of the effects needs the clarification of the structure of the dots, i.e., the dot size and the surface conditions. From a practical point of view (e.g., nanolaser), investigations of the structural origin behind the weak excitonic recombination is instructive for exploring strong UV light from ZnO QDs. In this work, we attempted to change the structure of the dots by an annealing process. Here, we report the effect of such changes on the luminescence properties.

Free standing ZnO QDs powder was prepared by the reaction of Zn²⁺ with OH⁻ in methanol, based on the dehydrating properties of the alcohol. Detailed work is reported elsewhere.¹⁰ The samples used in this work were obtained by annealing the powder in air at different temperatures from 150 °C–500 °C for 30 min. In comparison, highly purified bulk ZnO powder (Aldrich Co.), Zn(OH)₂, and Zn(OH)₂ (150 °C), i.e., Zn(OH)₂ sample annealed in air at 150 °C for 30 min, were studied as reference samples. Zn(OH)₂ was obtained by mixing Zn(NO₃)₂ and NaOH aqueous solution. It is known from the textbook chemistry that Zn(OH)₂ prepared in this way is amorphous.

The samples were characterized by x-ray diffraction (XRD), optical absorption, and Raman measurements. For absorption measurement, the powder samples were dispersed

in water with the help of an ultrasonic treatment. Room temperature photoluminescence (PL) was excited by the 325 nm line of a He–Cd laser. All the characterizations were carried out on the freshly prepared samples.

Figure 1 shows the XRD pattern of ZnO quantum dots and the reference samples. In the as-prepared unannealed sample (curve a), the diffraction peaks related to wurtzite ZnO are considerably broad. Upon annealing the diffraction peaks become more intense and narrower (see curve b), indicating increasing crystallinity and size. The average size of the particles can be estimated from the halfwidth of the diffraction peaks applying the Scherrer formula, and is approximately 4.3 nm in diameter for the unannealed sample, and are 4.8 nm, 5.3 nm, and 7.0 nm for the sample annealed at 150 °C, 300 °C, and 500 °C, respectively. However, after exposure to humid air for one month, the diffraction peaks become much weaker and broader (see curves a' and b') (a discussion is presented next). In addition to the ZnO diffraction pattern, a peak at 59.5°, as indicated by the arrow in Fig.

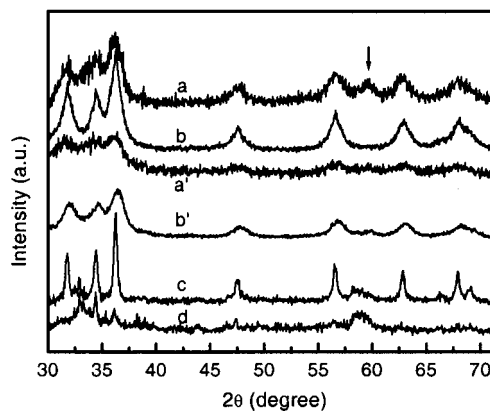


FIG. 1. XRD pattern of ZnO QDs (a, b, a', and b') and reference samples (c,d): fresh unannealed (a); annealed at 500 °C (b); (a) exposed to humid air for one month (a'); (b) exposed to air for one month (b'); Zn(OH)₂ (150 °C) (c); Zn(OH)₂ (d).

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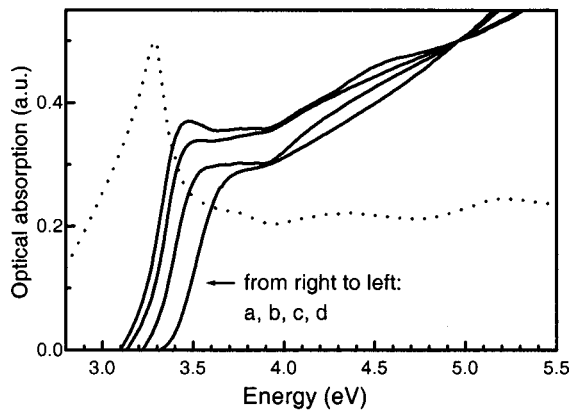


FIG. 2. Optical absorption of ZnO QDs (a)–(d) and reference bulk ZnO (dotted line): unannealed (a); annealed at 150 °C (b); 300 °C (c); 500 °C (d). The spectra of the dots have been normalized at 250 nm.

1, is observed. It decreases upon annealing and vanishes above 300 °C. A diffraction peak at the same angle is also present in the XRD spectrum of the freshly prepared $\text{Zn}(\text{OH})_2$, and this makes it very likely that it is related to $\text{Zn}(\text{OH})_2$. In the $\text{Zn}(\text{OH})_2$ (150 °C) sample, the 59.5° diffraction peak decreases, and sharp ZnO peaks appear. The linewidth gives evidence that in this case rather large ZnO particles (≈ 24 nm) are formed.

The growth of ZnO QDs is also shown by the optical absorption spectra (Fig. 2). The unannealed dots exhibit the band to band absorption at 3.82 eV at an energy substantially higher than that of the ZnO bulk reference sample (dotted line in Fig. 2) which shows excitonic absorption at 3.29 eV. Upon annealing, the absorption of the dot shifts to lower energies, indicating the growth of the size. According to the effective mass approximation,¹¹ we can use the energy position to estimate the average particle size. With the effective masses of electrons ($m_e = 0.28 m_0$, where m_0 is the free electron mass) and holes ($m_h = 0.59 m_0$) taken from Ref. 12, we obtain 4.2 nm for the as-prepared dots and for the dots annealed at 150 °C, 300 °C, and 500 °C the average diameters of 4.9 nm, 5.4 nm, and 6.5 nm, respectively. These results are in very good agreement with the diameters obtained from the XRD data. The size distribution which can be estimated from the width of the absorption peaks is about $\pm 15\%$, as also confirmed by our transmission electron microscopy observation.¹³

The existence of $\text{Zn}(\text{OH})_2$ in ZnO QDs, or at least that of OH groups, is demonstrated by Raman spectroscopy (Fig. 3). In the range from 3200 to 3600 cm^{-1} , where the OH stretching mode should appear, we observe a strong broad and unstructured band in the as-prepared QDs, while no signal is seen in the reference bulk ZnO. Upon annealing, the intensity of this band rapidly decreases (inset in Fig. 3). At lower energies, we find the modes of the lattice vibrations of wurtzite ZnO (E_2 at 439 cm^{-1} , A_1 [longitudinal optical (LO)] at 577 cm^{-1} , and combination modes of LO and transverse optical modes at higher energies). Details of this part of the spectra, especially the influence of the quantum size effect on the ZnO lattice vibrations will be published elsewhere.¹³ The important point here is that there exists $\text{Zn}(\text{OH})_2$ in the as-prepared ZnO QDs and upon annealing it

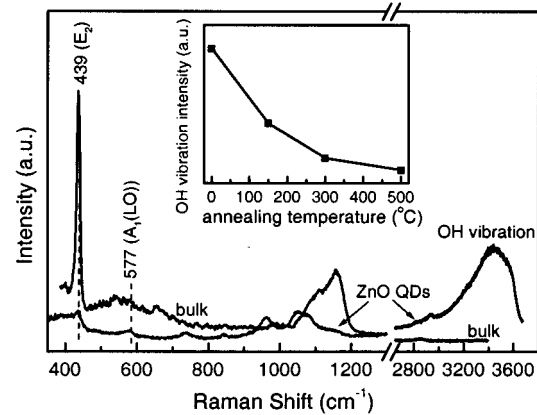


FIG. 3. Raman spectra of ZnO QDs and bulk ZnO. The inset shows the change of the OH vibration at 3400 cm^{-1} upon annealing temperature.

is gradually released while the size of the ZnO QDs increases.

Figure 4 shows the room temperature PL spectra of the ZnO QDs and the reference samples. The spectra in the visible region are fitted by Gaussian bands, as shown by the dotted lines in Fig. 4. For the as-prepared unannealed ZnO dots (curve a), the green luminescence band with a maximum at 2.34 eV is very strong, while the UV peak around 3.32 eV is much weaker. The intensity ratio is around 0.09. Upon annealing at 150 °C, the UV band increases in intensity to a ratio around 0.35 and redshifts to 3.28 eV, while the green band shifts to 2.25 eV and a weak alternate band at 2.71 eV appears (curve b). For the sample annealed at 300 °C, the UV band continues to increase and evolves into an prominent sharp peak at 3.25 eV (curve c). The green band redshifts to 2.20 eV, and the alternate band reaches maximum intensity. With a further increase in the annealing temperature, the ratio of the UV to the green band continuously increases (curve d). The spectrum is reproduced by two

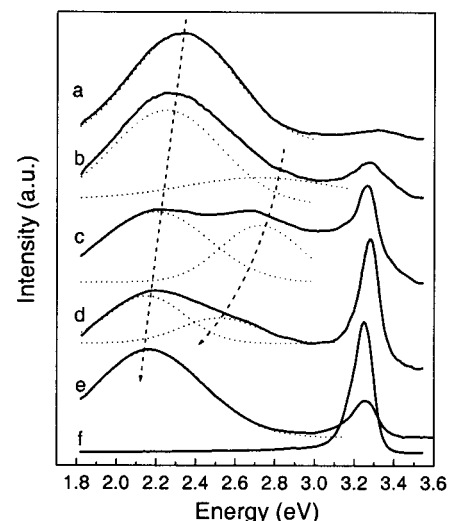


FIG. 4. PL spectra of the corresponding ZnO QDs (a)–(d) as in Fig. 2 and reference samples (e,f) at room temperature: $\text{Zn}(\text{OH})_2$ (150 °C) (e); ZnO bulk (f). The dotted lines are the fitted Gaussian bands. The dash curves with arrows are guided for eyes.

transitions centered at 2.15 and 2.52 eV. No PL from 3.3 eV down to 1.8 eV was detected for Zn(OH)₂ powder. For the Zn(OH)₂ (150 °C) sample, the weak UV band and the strong visible band at 2.16 eV (curve e) should come from ZnO with much larger particle sizes. Only the UV emission at 3.21 eV is observed for the bulk OH-group free ZnO (curve f). It thus seems that, for ZnO QDs, the appearance of strong UV emission is closely related to the annealing process. In addition to the strong increase of the UV emission, the annealing treatment also introduces new emission bands in the visible region and causes a redshift of all visible bands.

We now discuss the appearance of the strong UV emission in ZnO QDs. As the dot size grows with annealing, it might be concluded that the strong UV emission is related to bigger particle size. If this would be the case, even stronger UV emission should have been observed for the reference Zn(OH)₂ (150 °C) sample, i.e., ZnO dots with much bigger size (24 nm in diameter). This is however in contradiction with the observation (see curve e in Fig. 4). In addition, earlier work showed that the UV band increases very slightly with increasing particle size and the green band remains dominant (see Ref. 5). It is therefore not sufficient to correlate the strong UV emission in this work only with the growth of the particles.

Considering the presence of Zn(OH)₂ in ZnO QDs, it is reasonable to propose that Zn(OH)₂ forms a thin layer on the surface of ZnO QDs, thus forms a ZnO/Zn(OH)₂ core-shell structure. (One might argue for the existence of Zn(OH)₂ nanoparticles. However, such a chance would be very slim because of the preparation method, i.e., the dehydration properties of the alcohol.) Since ZnO is extremely sensitive to H₂O environment,¹⁴ the situation in ZnO QDs should be even more severe. To investigate the surface effect, we exposed the annealed dots to two different ambience for one month: one was dry N₂, the other was humid air. It was found that the dots stored in dry N₂ maintained the same properties as the fresh ones. For those exposed to humid air, compared with the original states, even weaker and broader XRD patterns were obtained (see curves a' and b' in Fig. 1), indicating decreasing crystallinity and size. The decrease of the UV emission intensity with blueshift of the PL was observed. Upon annealing, we were able to restore the PL again. This study proves that the surfaces of the dots are passivated by Zn(OH)₂ and shows that the outer layer grows by consuming some ZnO from the core. The thickness of the shell is roughly estimated to be in the range of 0.5–1.3 nm by comparing the sizes of ZnO QDs before and after annealing.

Based on the aforementioned results, we suggest that the weak excitonic transition of ZnO QDs is strongly correlated with the presence of the surface shell of Zn(OH)₂. When the

Zn(OH)₂ shell is present, the excitonic emission from ZnO QDs is suppressed. This is perhaps the reason why strong UV emission was not observed before in the as-prepared unannealed and not intentionally surface capped ZnO QDs by other groups with the similar method. The observations of strong UV luminescence from surface capped OH free ZnO QDs^{3,4} give convincing support to our model. The weak UV emission in the Zn(OH)₂ (150 °C) sample is then also due to the presence of large amount of Zn(OH)₂ on the surface of the big ZnO particles. However, the details of the bonding of the Zn(OH)₂ shell to the ZnO core, leading to the quenching of the ZnO excitonic emission in ZnO are not clear yet. Further work is in progress.

With the core-shell model, we can now explain the appearance of an alternate band. It is attributed to the decomposition of the surface Zn(OH)₂ (when the temperature is higher than 125 °C), which nucleates to alternate small ZnO clusters and grows upon annealing. The redshift of this band and the original green band can be well explained according to the size-dependent luminescence,¹⁵ i.e., the emission energy of a QD strongly depends on its size.

In summary, we have investigated the effect of different processing conditions on the luminescence properties of ZnO QDs. We provide strong evidence that the dots consist of a ZnO/Zn(OH)₂ core-shell structure. When Zn(OH)₂ is present, the excitonic transition of ZnO QDs is quenched. This is probably the main reason behind the commonly reported weak excitonic emission of ZnO QDs where the surface is capped by Zn(OH)₂. Strong UV emission is observed for dots annealed at high temperatures, when the outer shell of Zn(OH)₂ is released.

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